Cathodic Protection of Aluzinc coated, Galvanized and Stainless Steels in Ijegun Seawater using Aluminium as Sacrificial Anode

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Abstract— Cathodic protection is an electrochemical method of controlling corrosion on metallic structures which are in electrolytes. Safety and environmental aspects of corrosion are difficult to quantify in terms of costs but are known to have put people's lives at risk hence this research aimed at the study of cathodic protection of aluzinc coated, galvanized and stainless steels with aluminium as the sacrificial anode in Ijegun seawater. The samples (300 x 50 x 2 mm3) were connected independently to the sacrificial anodes of Al with cables and then submerged in Ijegun for 16 weeks. All samples were characterized by Scanning Electron Microscope. The corrosion rates were determined by gravimetric and electrochemical impedance spectroscopic methods. The gravimetric method results showed the corrosion rate of protected samples: stainless, galvanized and aluzinc coated steels were 2.54E-4, 4.84E-4 and 1.80E-3 mm/yr respectively while the control samples were 5.36E-4, 9.55E-4 and 3.97E-3 mm/yr in that order. The electrochemical impedance spectroscopic results obtained for protected stainless, galvanized and aluzinc coated steels were (629.351, 685.575), (268.786, 253.498) and (216.3464, 58.380) Ω respectively while the control samples were (527.417, 299.112), (188.150, 91.259) and (66.3077, 24.022) Ω in that order. The scanning electron microscope results showed thicker masses on unprotected than protected samples. The methods used revealed that, stainless steel had the highest resistance to corrosion while aluzinc coated steel had the least resistance. Conclusively, cathodic protection method using sacrificial anode of aluminum is effective in protecting steels in marine environment.

Keywords— Al as sacrificial anode, cathodic protection, EIS, gravimetric evaluation, potentiodynamic polarization, steels.

INTRODUCTION

Cathodic protection is a method of protecting metallic structures that are in electrolytes using electrochemical means (Arif et al. 2018 & James 200). Earlier researcher like Volkan (2013) reported that an external protective current must be applied to the metal to be protected by cathodic protection technique such that the potential of the metal has to be polarized to the point of the anode's open circuit potential as well as adjusting the anodic protective currents to zero. Cathodic protection is a method by which the surface of metal is replaced as cathode electrode in an electrochemical cell in order to control the corrosion. The application of cathodic protection has gone viral in protecting submerged engineering equipment in water or underground such as ship hulls and interiors, vessels, pipeline, lead cables, lock gates and dams and water treatment equipment (James, 2000). The basic four components of corrosion processes are; electrolyte, electronic path, cathodic reaction, and anodic reaction, virtually corrosion control would be impossible if any of these components is missing out. The ionic charge is being transferred into an aqueous solution for most of metallic corrosion process. Cathodic protection played major role in enhancing durability of seawater applications including submerged structures (Nestor, 2004). Cathodic protection is highly practicable in preventing corrosion on metals generally both in soils and aqueous media. This can be done by connecting an external anode that can be in form of galvanic (sacrificial) anode or as an impressed protective current anode to the protecting material and protective current is generated which then disallows corrosion to take place as reported by Adetunji et al. (2019) and others (Rashid 2009; Ramezanzadeh et al. 2010 & Padilla and Alfantazi 2014). There are three main anodes being used as sacrificial anodes: magnesium, aluminum and zinc for cathodic protection, many researchers have proved that in protecting steel by cathodic protection method, zinc alloys are preferred to

other two as results of affordable cost, minimum specific weight with maximum protective current efficiency (Oloruntoba et al. 2009; Kuang et al. 2010; Baeckmann et al. 1997 & Hajar et al. 2016).

The outcome of time taken for the cathodic protection of carbon steel pipe submerged in 0.1N NaCl by varying the temperatures has been studied by Slaiman and Hasan (2010). The result showed that the protective potential was inversely proportional to time. In their experiment set up for four hours and at first hour the potential became more negative taking record at every 15 minutes while the curve reached asymptotic value at -990, -990 and -1070 mV versus standard calomel electrode, which represents the protection potential for 55, 45 and 35 °C in that order (Ross et al. 1996). Studies showed that corrosion potential (V) is mostly controlled by the level of concentration of oxidizer. In seawater or slightly salted water, aluminum anode is preferably selected for cathodic protection of metallic samples. When the aluminum anode has copper and nickels in its composition, its potential moves toward positive direction while the composition of zinc, magnesium, and cadmium with aluminum anode decreases the passivation and moves the potential in the positive direction likewise. In addition, the aluminum anode with constituents of mercury, tin, and indium makes it very active at all times which ends to uniform dissolution (Kuang et al. 2010 & Volkan 2013). Considering the electromotive force series, ideally aluminum is more active than zinc; aluminum surface appears naturally with protective oxide films that hindered it to be used as anode until 1950s with potential of -900 mV in comparison with the value of reference electrode in seawater. After a while, the protective current efficiency and potential of aluminum anodes increased up to 50% and -1.3V respectively when 3% of zinc and 5% of tin elements were added. The protective current efficiency and the potential also increased up to 90 % and -1.05 V respectively when zinc and mercury elements were added to aluminum (Volkan 2013). Protection and environmental aspects of corrosion are very hard to quantify in terms of costs but are known to have put lives and structures at risk hence this research studied the cathodic protection of galvanized, aluzinc coated and stainless steels in Ijegun seawater.

MATERIALS AND METHOD
2.1 Sample preparation
The samples of dimensions 300 x 50 x 2 mm3 made from aluzinc coated steel, galvanized steel and stainless steel (type 304, A2) were cut from parent materials, they were mechanically polished using 400 and 1200 emery paper. The polished samples were cleaned with acetone, washed using distilled water and dry-cleaned with tissue paper before and after submersion in the seawater. The aluminium anodes were electrically connected independently to the surfaces of the dimensioned samples that were to be cathodically protected with the aid of cables. They were all arranged in perforated big plastic containers and then submerged in Ijegun while the controls were also submerged at the same time for duration of 16 weeks. The corrosion rates of the samples were determined by gravimetric, electrochemical impedance spectroscopy and polarization techniques (TCH 1999).

2.2 Gravimetric Method
The prepared samples were weighed that is, before submersion as the initial weights w1(g) by digital weighing balance model number AG-TT (weighing capacity 0-30Kg). Also, after elapsed submersion times, the samples were cleaned from fouling organisms/ calcium deposit, rinsed with acetone, washed using distilled water and dry-cleaned with tissue paper and then weighted as final weights of w2 (g). The differences in weights were taken as weight loss to determine the corrosion rate.

2.3 Potentiodynamic Techniques
The tests run using the potentiostat are potentiodynamic to generate polarization curves for each of the steels. The potentiodynamic test involved a "sweep" in which the potential is increased at a linear rate until an upper limit is reached. During the sweep, the resultant current was monitored and plotted in real time. A typical sweep rate is around 10 mV/minute (0.6 V/hour) (Yan et al. 1992). However, for each experimental setup the sweep rate should be maximized to find the fastest scanning rate without altering the results (generally accepted practice is changing the data by less than a factor of 2).

The generated polarization curve plots the potential in volts against log current. Tafel fit lines are then placed on the graph on both the cathodic and anodic reaction sections; the intersecting point of the two Tafel curves is the open-circuit potential (e.m.f. value) (Lana et al. 2006).

The measurements of polarization were presented in the form of Tafel plot; results show the values of corrosion potential (Ecorr) shifted more to the positive direction as the presence of henna extract. At room temperature and at 50 °C, the Ecorr value increase as there is presence of henna which is -0.34368 V/SCE to -0.18868 V/SCE and -0.45398 V/SCE to -0.38371 V/SCE respectively. Since The Ecorr shift toward more positive direction and

indicates that henna is a mixed-type inhibitor. However, the Ecorr value drop to -0.30495 V/SCE at room temperature and 0.38972 V as the henna percentage increase to 20 %. In addition of henna percentage, the corrosion potential Ecorr values shift to the range (0.12-0.16) V/SCE. The higher value of corrosion potential indicates lower corrosion rate.

The general experimental arrangement for electrochemical impedance spectroscopy (EIS) testing contains a glass spherical joint with a rubber 'o' ring seal are clamped onto surface of the sample to be examined. A platinum sheet and calomel electrode suspended in the electrolyte served as counter and reference electrodes respectively, with the material to be tested as the working electrode. A carbon fiber/vinyl ester composite in 3.5 % NaCl solution was used. Impedance measurement was performed by a PAR 273 potentiostat conjunction with an IBM personal computer and a

Solartron 1255 high frequency response analyzer (FRA), with PARC 388 unprotected software. Electrochemical impedance spectroscopy (EIS) measurement was carried out for a frequency range of 100 kHz to 10 mHz, with applied 10 mV sinusoidal potential around the open circuit potential. The polarization curves were derived from open circuit potential −200 to +200mV and the scan rate was 0.5 mV/s (Harvey 1995).

2.4 Conducting Environment

The study was carried out at Ijegun seawater site, Lagos, Nigeria, this served as the electrolyte medium with details analysis was determined by Digital Refractometer machine.

2.5 Anodic Protective Efficiency

To estimate protective efficiency of aluminium used as sacrificial anode is stated in equation 1,

$$Anodic\ Protective\ efficiency = \frac{Corrosion\ rate\ of\ unprotected - Corrosion\ rate\ of\ protected\ sample}{Corrosion\ rate\ of\ unprotected\ sample} x100\%$$

$$= 1 - \frac{CR_{protected\ sample}}{CR_{unprotected\ sample}} x\ 100\%$$

2.6 Characterization of Samples

All samples were characterized by Scanning Electron Microscopy machine)SEM(to examine the surface cross sectional analyses, X-ray Diffractometer machine)XRD(to determine the mineral constituents while the seawater analysis was carried out by Digital Refractometer machine.

2.6.1 SEM sample preparation

The SEM machine with model JEOL-JSM 7600F was used to determine the morphologies of the samples. All samples were dimensioned to 6-inch)15 cm(semiconductors wafers that were appropriate sizes to fit in the specimen chamber and were generally mounted rigidly on a specimen holder called a specimen stub with tilt angle of 450.

Samples were coated with ultrathin coating of electrically conducting material, deposited on the sample either by low-vacuum sputter coating or by high-vacuum evaporation. SEM instruments place the

specimen in a relative high-pressure chamber where the working distance is short and the electron optical column is differentially pumped to keep vacuum adequately low at the electron gun. The high-pressure region around the sample in the SEM neutralizes charge and provides an amplification of the secondary electron signal.

RESULTS AND DISCUSSIONS

3.1 Analysis of Seawaters Used

Table 1 displayed the analysis of marine water)Ijegun seaport(used as the electrolyte for this research been determined by Digital Refractometer machine. Ijegun seaport is located in Amuwo Odofin local government area of Lagos State, Nigeria.

It was shown that the major constituents influencing corrosion attack in the seawater had the following parameters with their values: pH, conductivity, temperature, acidity, chloride and salinity of the seawater were 6.92, 2570 µs/cm, 24.51 oC, 80.04, 814.83 and 1.69 mg/l respectively.

Table 1. The Analysis of Ijegun Seawater

Parameters	pH	Conductivity)µs/cm(	Saliniy)mg/l(	Temperature)oC(	TDS)mg/l(	Acidity	Alkalinity	Cl-	Na	Ca	Mg
Values	6.92	2570	1.69	24.51	1504	80.04	250	814.83	12	65.05	2.14

Table 2. Percentage of Chemical Compositions of the Steels used

Elements)%(/ Steels	Mn	Fe	Cr	S	C	Mo	Ni	P	Si	Zn	Al
Stainless)SS(	1.40	82.94	10.01		0.07	1.20	4.00		0.38		
Galvanized)GS(	0.80	87.78		0.04	0.14			0.044		11.20	
Aluzinc coated)AZS(					0.02				1.50	43.48	55.00

Table 3. Percentage of Chemical Composition of Aluminium Anode

Elements (%)	Mn	Fe	Si	Cu	Al	Zn
Al Anode	0.01	0.08	0.12	0.044	96.246	3.50

3.2 Chemical Compositions of Aluzinc coated steel, Galvanized steel, Stainless steel and Sacrificial anode

Table 2 exhibits the percentage of chemical compositions of aluzinc coated, stainless and galvanized steels. The major two elements that were present in stainless steel were iron and chromium for 82.94 and 10.01 % respectively while galvanized steel had iron and zinc as the two major constituents for 87.78 and 11.20 % respectively and aluzinc coated steel had two main constituents of aluminium and zinc with the values of 55 and 43.48 % respectively. Table 3 shows the percentage of chemical composition of aluminium anode that was used for the study. The sacrificial anode of aluminium used had certain degree of purity since the percentages of all trace elements were less than 4 % and the percentage of composition of purity for sacrificial anode of aluminium was 96.246 %.

3.3 The Gravimetric difference obtained from Steels been submerged into Ijegun Seawater

Table 4 shows the gravimetric differences from the stainless, galvanized and aluzinc coated steels that were connected with and without sacrificial anode of aluminium which has been submerged in Ijegun seawater from zero hour to 2688 hours. It was observed generally that the weight loss of the three protected steels (SS+Al, GS+Al and AZS+Al) increased steadily as the submersion times increased (Owoeye et al. 2020). Also the values of weight loss for unprotected samples that is the controls (CSS, CGS and CAZS) were more than twice the values of corresponding protected samples. This displayed that anode play a vital role as the deterioration of samples were greatly reduced compare to unprotected samples. The values of weight loss of SS+Al, GS+Al and AZS+Al at initial and final submersion times were 0.08 and 0.18 g; 0.20 and 0.35 g; and 0.3 and 0.63 g respectively. Also the values of weight loss at first and last submersion times of CSS, CGS and CAZS were 0.20 and 0.35 g; 0.44 and 0.69 g; and 1.00 and 1.39 g respectively.

The compositions of each sample used in this study played a vital role in resisting the deterioration has been submerged in seawater. The stainless steel that had the highest resistance to corrosion among the three samples used was due to the presence of chromium (Anees et al. 1999). The presence of carbon element in all the three samples used with reasonable percentage also helped the hardness of such materials from pitting corrosion. It was observed that the resistance to dissipation of stainless, galvanized and aluzinc coated steels decreased in that order.

Table 4. Weight Loss of the Submerged Steels into Ijegun Seawater

Samples	WL(g) 336Hrs	WL(g) 673Hrs	WL(g) 1008Hrs	WL(g) 1344Hrs	WL(g) 1680Hrs	WL(g) 2016Hrs	WL(g) 2352Hrs	WL(g) 2688Hrs
SS+Al	0.08	0.09	0.11	0.12	0.13	0.15	0.16	0.18
GS+Al	0.20	0.22	0.24	0.27	0.29	0.31	0.33	0.35
AZS+Al	0.30	0.34	0.38	0.43	0.47	0.51	0.55	0.63
CSS	0.20	0.22	0.25	0.27	0.29	0.32	0.35	0.38
CGS	0.44	0.47	0.51	0.55	0.58	0.61	0.64	0.69
CAZS	1.00	1.05	1.11	1.16	1.22	1.27	1.33	1.39

3.4 Corrosion Rates of Protected samples by Aluminium Anode and the Control

The corrosion rate of stainless, galvanized and aluzinc coated steels that were protected by sacrificial anode of aluminium (SS+Al, GS+Al and AZS) and the controls (CSS, CGS and CAZS) been submerged in Ijegun seawater is displayed in Table 5 while the graphical the representation is shown in Fig.1. It was noticed

generally that the highest values of corrosion rates of all samples were at first submersion time and declined gradually as the submersion times increased. The corrosion rates of SS+Al, GS+Al and AZS+Al samples at first time of submersion time were 0.000903, 0.002214 and 0.006861 mm/yr respectively while the corrosion rates at final submersion time were 0.000254, 0.000484 and 0.001801 mm/yr in that order. Also the values of corrosion rates of the controls (CSS, CGS and CAZS) at first were 0.002257, 0.004871 and 0.022870 mm/yr respectively while at last submersion times were 0.000536, 0.000955 and 0.003974 mm/yr in that order. It was noticed that the aluminium anode helped in reducing the rate of deterioration of the three samples compared to the control samples. It was observed also that the stainless steel had the highest resistance to corrosion while aluzinc coated sample had the lowest resistance to corrosion. It was observed generally that

cathodic protection technique for protecting steel samples in seawater environment was feasible in which more electrons were supplied from the sacrificial anode to the samples as cathodic reaction in which oxygen was drained out with evolution of hydrogen (Lavanya et al. 2018).
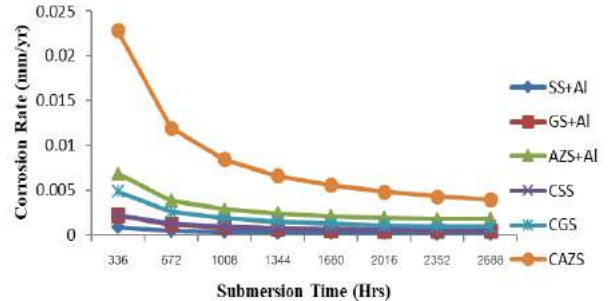
Figure 1. Graph of Corrosion Rate of steels protected with and without sacrificial anode of Al

Table 5. Corrosion rates of protected and control steels by aluminium anode

Samples	CR (mm/yr) at 336Hr	CR (mm/yr) at 672Hr	CR (mm/yr) at 1008Hr	CR (mm/yr) at 1344Hr	CR (mm/yr) at 1680Hr	CR (mm/yr) at 2016Hr	CR (mm/yr) at 2352Hr	CR (mm/yr) at 2688Hr
SS+Al	0.000903	0.000508	0.000414	0.000339	0.000293	0.000282	0.000258	0.000254
GS+Al	0.002214	0.001218	0.000886	0.000747	0.000642	0.000572	0.000522	0.000484
AZS+Al	0.006861	0.003888	0.002897	0.002458	0.002150	0.001944	0.001797	0.001801
CSS	0.002257	0.001241	0.000941	0.000762	0.000655	0.000602	0.000564	0.000536
CGS	0.004871	0.002602	0.001882	0.001522	0.001284	0.001126	0.001012	0.000955
CAZS	0.022870	0.012007	0.008462	0.006632	0.005580	0.004841	0.004345	0.003974

3.5 Electrochemical Impedance Spectroscopy (EIS) for Protected and Control Samples

Fig. 2, (A) displays the electrochemical impedance spectroscopy of the protected stainless, galvanized and aluzinc coated steels by sacrificial anode of aluminium in which imaginary impedance was plotted against the real impedance. From the graph stainless steel with highest frequency and phase angle which indicates the magnitude of impedance, had the highest resistance to corrosion, it was followed by galvanized steel while aluzinc coated steel with the least values of frequency and phase angle had the least resistance to corrosion which made it to be very prone to corrosion. It was observed that the capability of resistance to corrosion of the stainless, galvanized and aluzinc coated steels decreased in that order. The graph shows that all the curves started from origin and increased steadily. The magnitudes impedances (as reported in coordinates) of the samples: stainless galvanized and aluzinc coated steels decreased steadily which were given as (629.351, 685.575), (268.786, 253.498) and (216.3464, 58.380) ohms respectively. Fig. 2, (B) showed the electrochemical impedance spectroscopy of the control samples in Ijegun seawater with fitting model. It was

noticed from the graph that the magnitudes impedances (in coordinates form) of the samples: stainless, galvanized and aluzinc coated steels reduced drastically due to absent of sacrificial anode which were given as (527.417, 299.112), (188.150, 91.259) and (66.3077, 24.022) ohms respectively. All the steels were highly susceptible to corrosion while the aluzinc coated samples were much more affected by corrosion attack due to the least magnitudes of impedance.
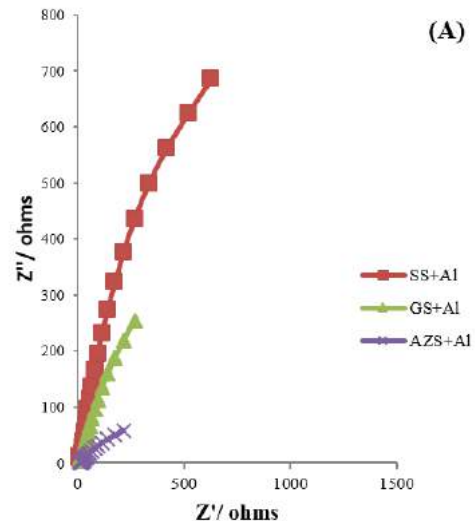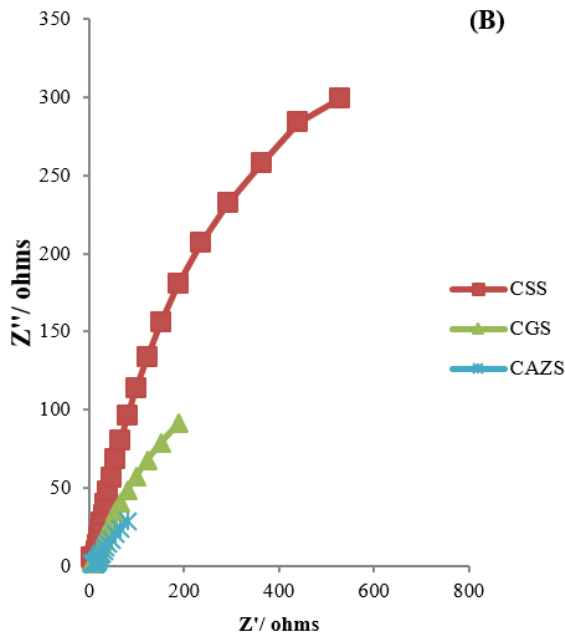
Figure 2. Graph of EIS of steels with sacrificial anode in Ijegun seawater

3.6 Polarization of the protected and unprotected samples

Electrochemical measurement is regarded as a fast and efficient technique which reflects the transient electrochemical process, so it could be used for determining and measuring corrosion rate on-site. 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 there is possibility of obtaining important information on the kinetics of the corrosion reactions. Electrochemical techniques for determining corrosion rate of sample materials, the total reduction and oxidation current densities were equal at the point where the cathodic line for the hydrogen evolution intersected the anodic line for metal dissolution reaction. The potential at which these lines intersected is termed the corrosion potential. In Fig. 3, (A) that showed the graph of corrosion potential of the tested samples that were protected by aluminium anodes against the current density, the polarization curves were not superimposed against one another. The highest resistance to corrosion was noticed on stainless steel with the value of corrosion potential of -0.8888 V and current density of 0.0935 A/cm2. The values of corrosion potential and current density for galvanized steel were -0.7217 V and 0.1131 A/cm2 respectively, which made it to be the second in resistance to corrosion while the least resistance to corrosion was noticed on aluzinc coated steel whose corrosion potential and current density were -0.5291 V and 0.1703 A/cm2 respectively. It could be stated that

from the chart that stainless steel had the least proneness to corrosion with the most negative value of corrosion potential (Ecorr) and the least current density. The aluzinc coated steel with the most positive value of corrosion potential and highest value of current density, observed to be the most affected sample by corrosion attack due to its least resistance to corrosion. The Tafel fit results for samples that were protected by sacrificial anode of aluminium is shown in Table 6. The susceptibility of samples to corrosion increased steadily in order of stainless, galvanized and aluzinc coated steels with corrosion rates of 0.002482, 0.016301 and 0.032012 mm/yr respectively (Rajappa 2008).

Fig. 3, (B) revealed the graph of corrosion potential of unprotected three samples against the current density, the polarization curves were not also superimposed against one another. 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 stainless, galvanized and aluzinc coated steels were -0.00277, -0.00238 and -0. 00190 V respectively while the values of current densities increased as 0.135, 0.173 and 0.281 A/cm2 in that order. In Table 7 which shows the Tafel fit results for the unprotected steels, the deterioration of steels was very significant on the steels with an increase in corrosion rates. The corrosion rate of the control samples: stainless, galvanized and aluzinc coated steels were 0.002482, 0.016301 and 0.041005 mm/yr respectively.
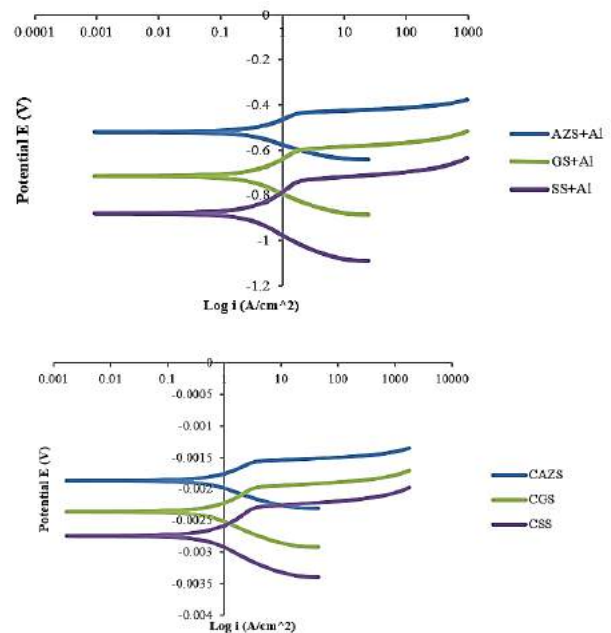

Figure 3. Polarization curves of protected samples by sacrificial anode of Aluminium in Ijegun seawater.

Table 6. Tafel Fit Results for Samples with Aluminium Anode

Samples	Ecorr (V)	Icorr (A/cm2)	C.R (mm/yr)	Remark on susceptibility to corrosion
SS+Al	-0.8888	0.0935	0.002482	Least affected
GS+ Al	-0.7217	0.1131	0.016301	More affected
AZC+Al	-0.5291	0.1703	0.041005	Most affected

Table 7. Tafel Fit Results for the unprotected Steels

Samples	Ecorr (V)	Icorr (A/cm2)	C.R (mm/yr)	Remark on susceptibility to corrosion
CSS	-0.00277	0.135	0.078889	Least affected
CGS	-0.00238	0.173	0.518205	More affected
CAZS	-0.0019	0.281	1.01766	Most affected

3.7 Anodic Protective Efficiency

The protective efficiency of anode in respect to the three cathodic materials been submerged in Ijegun seawater at the last day of submersion of 1680 hours is displayed in Table 8. It was observed that the highest efficiency was noticed on aluzinc coated steel while the least was on galvanized steel. The efficiencies of the three cathodic materials: stainless, galvanized and aluzinc coated steels been protected by Al anode were 55.27, 50.00 and 61.47 % respectively.

Table 8. Protective Efficiency of Aluminium Anode

Samples	Ɛijegun(%) at 1680Hrs
SS+Al	55.27
GS+Al	50.00
AZS+Al	61.47

3.8 Characterization of Steels
3.8.1 Scanning Electron Microscope

Fig. 4, (1A – 1C) exhibits the SEM of stainless steels for Fig. 4, (1A) as sample before submersion Fig. 4, (1B) as sample was protected by sacrificial anode of aluminium and Fig. 4, (1C) as control sample has been submerged in Ijegun seawater. Fig. 4, (1A) a showed repeated pattern of stainless steel atoms in crystalline forms, Fig. 4, (1B) showed conspicuous gray and white crystalline grains due to less effect of corrosion and Fig. 4, (1C) showed some clearer gray patches that covered ¾ portion of the image due to much effect of corrosion for unprotected sample. Fig. 4, (2A – 2C) displayed the SEM of galvanized steels in which Fig. 4, (2A) was before submersion, Fig. 4, (2B) for protected steel and Fig. 4, (2C) was the control sample been submerged in Ijegun seawater. The SEM of Fig. 4, (2A) was of galvanized steel before submersion showed a repeated pattern of crystals in the whole surface, Fig. 4, (2B) showed conspicuous crystalline grains while the control

sample exhibited some combination of gray patches with little white crystals on the sample surfaces due to deep corrosion attack. Fig. 4, (3A – 3C) which showed the SEM of Aluzinc coated steels where Fig. 4, (3A) was before submersion into Ijegun seawater, Fig. 4, (3B) for protected sample and Fig. 4, (3C) for control (unprotected) sample.

The SEM of Fig. 4, (3A) of aluzinc coated steel before submersion showed a continuous pattern of crystals in the whole surface, The SEM image of unprotected aluzinc coated steel showed gray and white patches throughout the surfaces for magnifications of 4,000. A serious corrosion attack was observed on the surfaces due to submersion without any cathodic protection (Owoeye et al. 2020). The aluzinc coated steel been protected when submerged in the marine environment showed pitting corrosion in the whole surface which was less intense than unprotected sample.
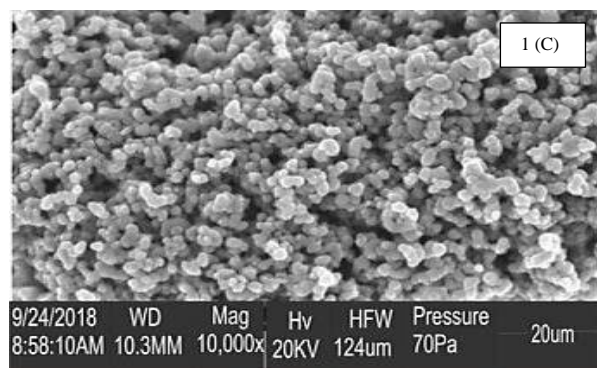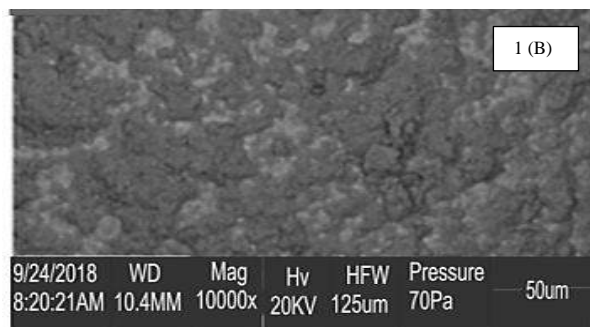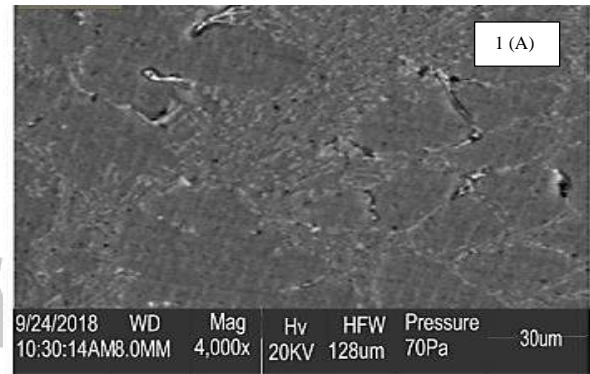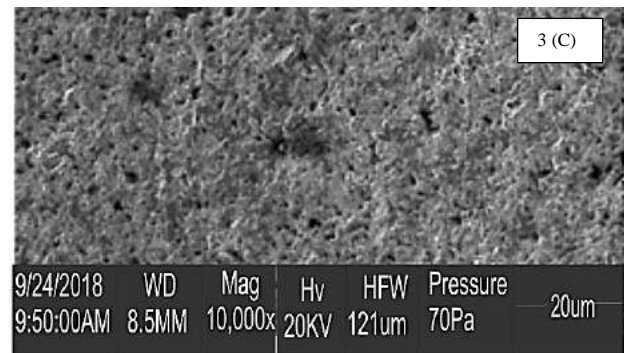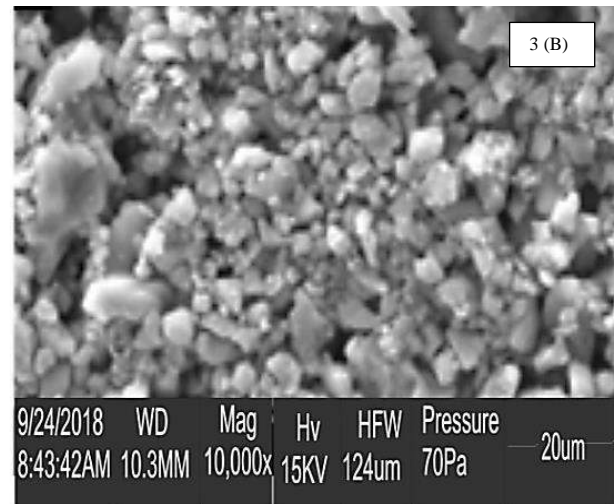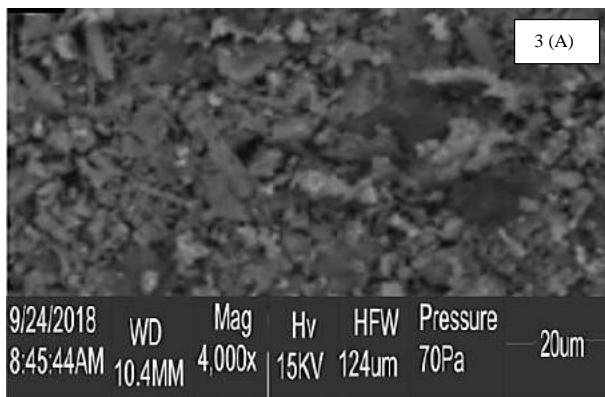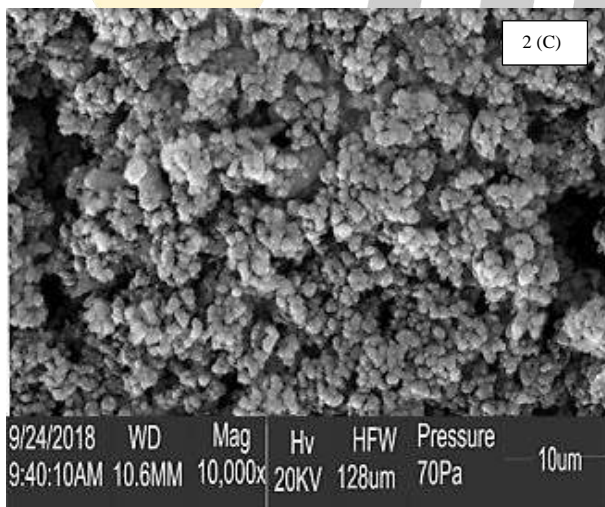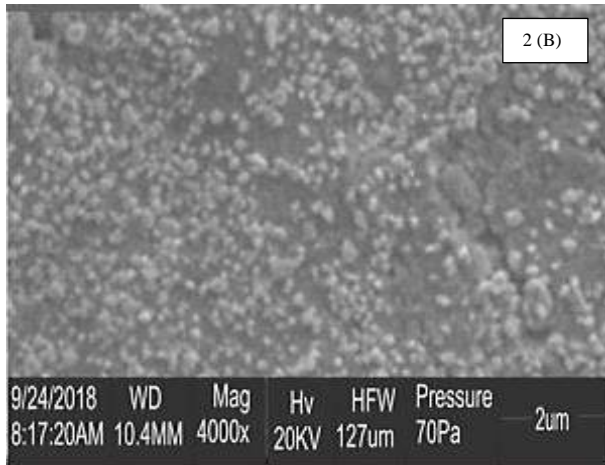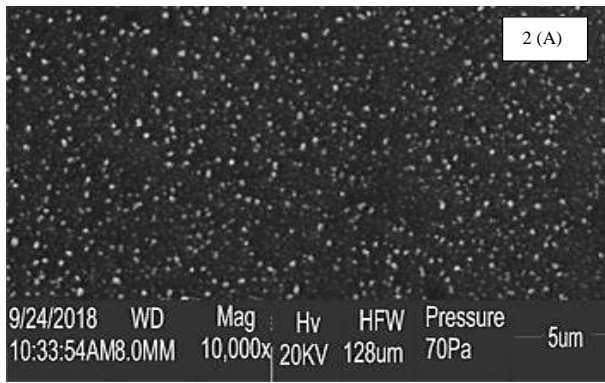
Figure 4. Scanning Electron Microscope; 1 = stainless steels, 2 = Galvanized steels, 3 = Aluzinc coated steels; A = before submersion, B = protected and C = control sample been submerged into Ijegun seawater.

3.8.2 Energy Disperse Spectroscopy

Fig. 5 showed the EDS analysis of stainless steels with Fig. 5, (A – C) for sample before submersion, unprotected and protected respectively been submerged in Ijegun seawater. Fig. 5, (A) gave percentage of chemical compositions as 0.18Si, 0.55Mn, 0.32C, 0.033P, 0.97Cr, 0.04S, 0.17Mo and 97.51Fe and after submersion some of the elements found before submersion were missing, some found reduced in percentage while others increased in percentage.

In Fig. 5, (B), the percentage of iron (Fe) reduced from 97.51 to 24.70 % due to corrosion attack; the sample was oxidized to 25.90 % of oxygen (O) and percentage of carbon increased from 0.32 to 13.50 % due to carbonation from microbial activities from the seawater (Neville 2002). Also in Fig. 5, (C) been protected had some traces of additional elements (Al and Mg) which could have come from the sacrificial anodes used in protection compared to natural state of the stainless steel. The percentage of major element: iron (Fe) reduced to 54.00 from 97.51 % while the carbon (C) only increased to 8.02 %.
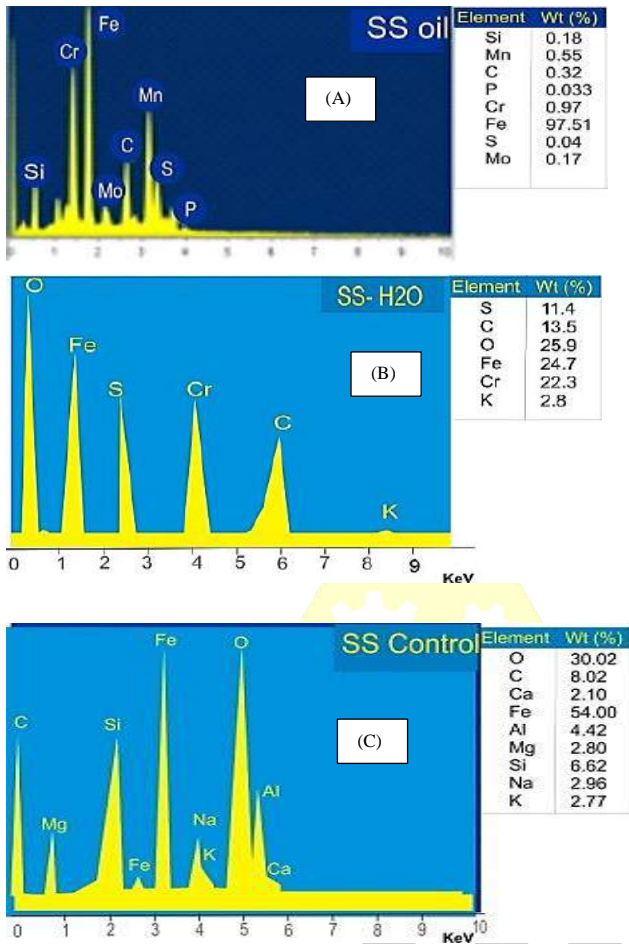
Figure 5. EDS of Stainless steel: a is sample before submersion b is unprotected sample c is cathodically protected sample submerged in Ijegun seawater

3.8.2 X-Ray Diffraction (X-RD)

X-Ray Diffractometer with Radicon MD-10UM of version 2.0, using CuKα radiation to analyse the phase from 11º<2θ<76º at exposure time of 1200/1200 seconds with Lambda: 1.5418 and Beta filter. Fig. 6, (A) showed the XRD patterns of stainless steel been submerged in Ijegun seawater which gave six peaks with the presence of iron and tetrataenite. Iron had the higher peak at 45° (2θ) and 3800 counts while the tetrataenite had its peaks at 44° (2θ) and 2100 counts, 51° (2θ) and 1800 counts and 74° (2θ) and 1900 counts.

Fig. 6, (B) showed the X-Ray Diffraction patterns of galvanized steel been submerged in Ijegun seawater with the presence of zinc, iron and zincite. The single and prominent pattern was superimposition of zinc and its compound (zincite) with peak at 46.4° (2θ) and 6000 counts while the other patterns were not pronounced. The diffusion process is often slowed down due to deposition of products at the anode and cathode plates, and hence, corrosion rate decreases (Möller 2006) Fig. 6, (C) exhibited the X-Ray Diffraction patterns of aluzinc coated steel been submerged in Ijegun seawater with the presence of iron and aluminium. There are five peaks in which three are for aluminium and the remaining two peaks are for combination of iron and aluminium. The highest peak was at 45° (2θ) and 5800 counts.
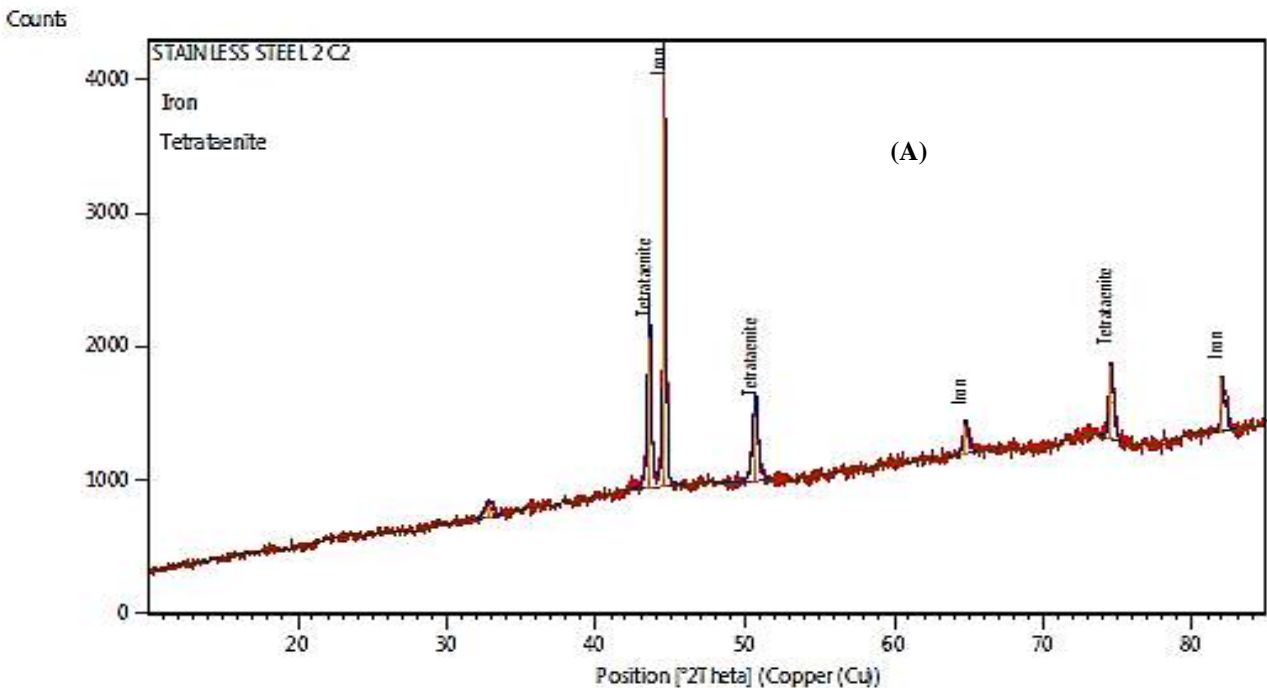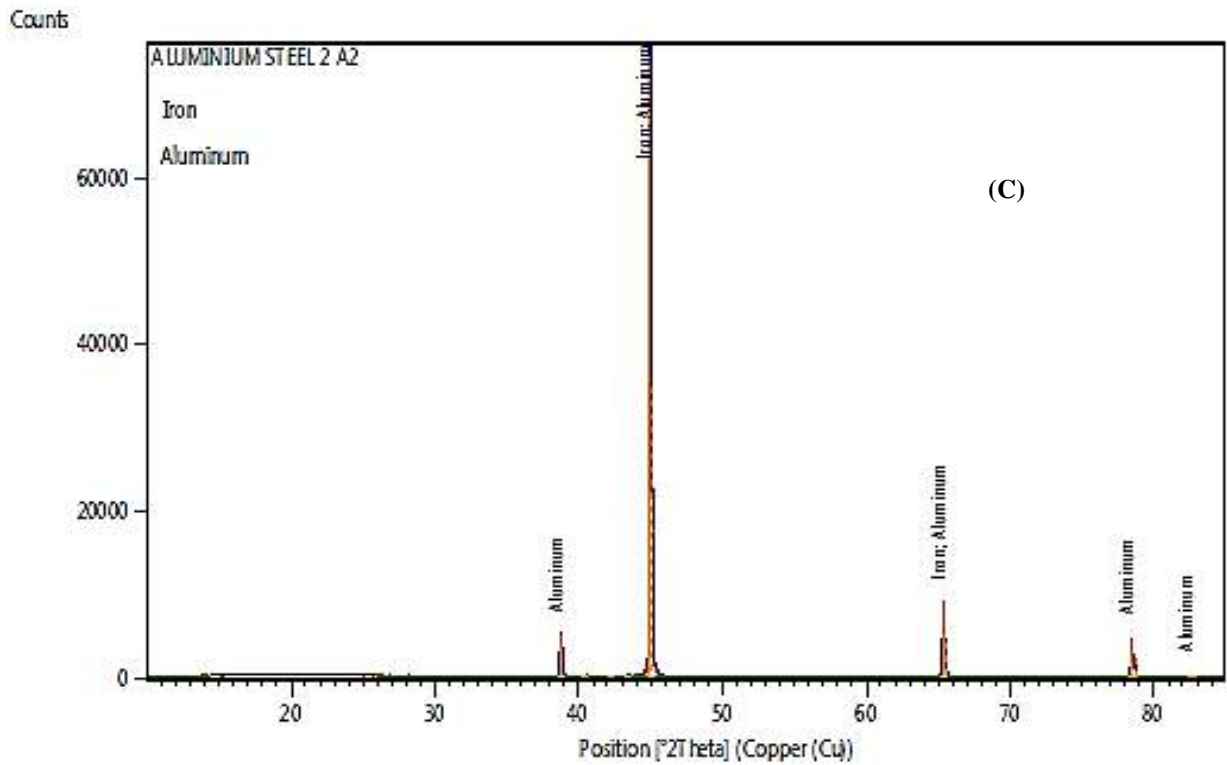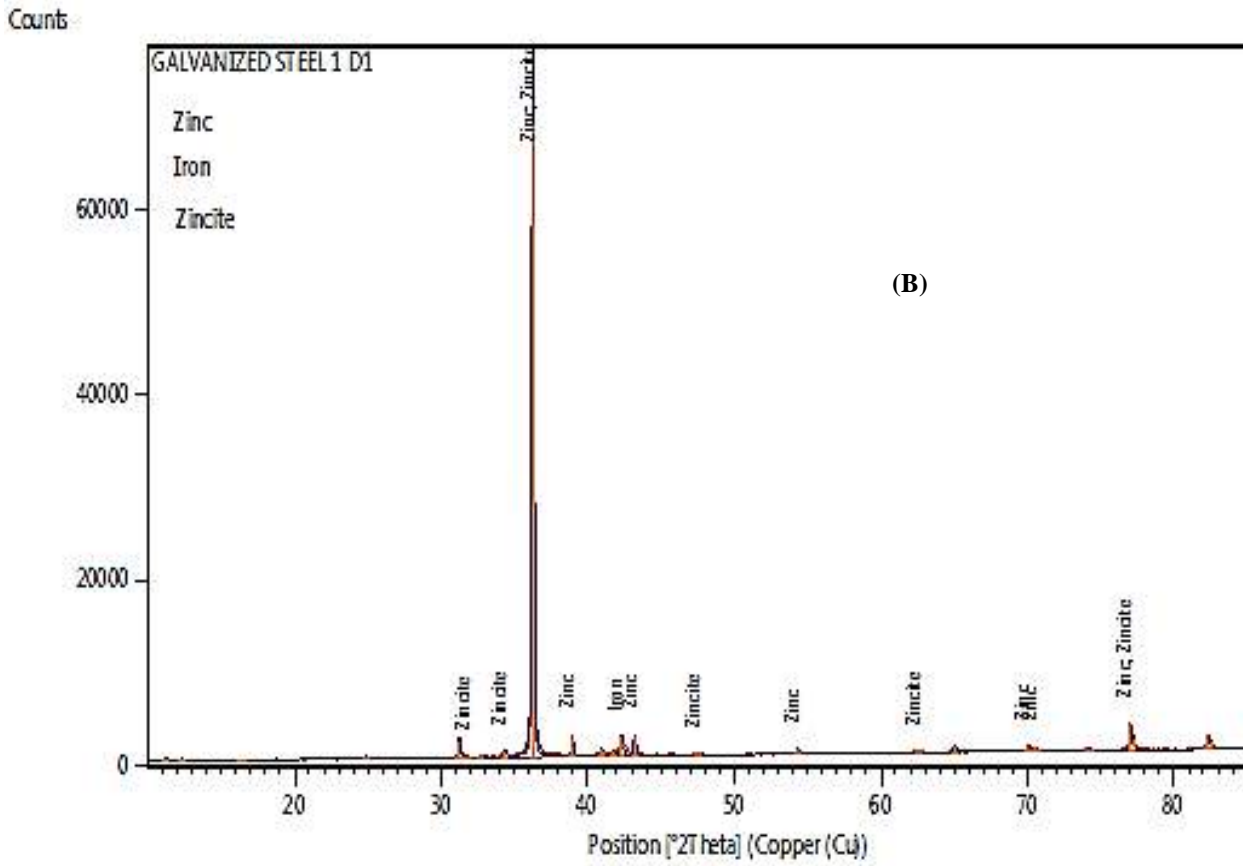
Figure 6. X-Ray Diffraction Pattern: A = stainless steel, B = galvanized steel and C= Aluzinc coated steel been submerged in Ijegun seawater

CONCLUSIONS

Having carried out the cathodic protection of aluzinc coated, galvanized and stainless steels in Ijegun seawater using Aluminium as sacrificial anode, the following findings are concluded;

- There was concurrence in the results obtained from the three techniques of gravimetry, potentiodynamic polarization and electrochemical impedance specroscopy used to determine the corrosion rate of the samples, the stainless steel had the least deterioration to corrosion than other two samples and aluzinc coated steel had the highest deterioration.
- The protective efficiency of aluminium anode used to protect the three cathodic materials were effective for galvanized steel, more effective for stainless steel and most effective for aluzinc coated steel in Ijegun seawater.
- The scanning electron microscope images of the protected and non-protected samples of aluzinc coated, galvanized and stainless steels showed pittings in non-protected samples.
- The XRD results of the corroded samples displayed the spectra of the elements present in the samples as the by-products of corrosion attacks.
- Cathodic protection produced evolution of hydrogen at the metal surface. Within the potential range for cathodic protection by aluminium production of hydrogen increases exponentially towards the negative potential limit.
- The weight of aluminum anode used reduced at final submersion time compared to initial weight and this was as a result of releasing electrons to protect cathodic materials
- The cathodic protection of some steels using sacrificial anode of aluminum is effective in reducing their deteriorations in marine environment.

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