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Corrosion Protection of Reinforced Concrete Steel Using Al and Zn Sacrificial Anodes in Marine Environment

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Abstract

Reinforced concrete is widely used in marine structures due to its strength and durability; the Rebar embedded in it is, however, very susceptible to corrosion when exposed to aggressive ions, such as chlorides from seawater. This research assessed the effectiveness of using aluminium and zinc sacrificial anodes for corrosion protection of steel in reinforced concrete exposed to marine environments. It involved embedding aluminium and zinc anodes in the concrete specimens and exposing them to a controlled marine environment. The surface profile of the steel was analysed using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). The results obtained showed corrosion rates of the steel reinforcement obtained were 1.002 mm/y, 0.562 mm/y, and 0.264 mm/y while the protection efficiencies rendered by the aluminium and the zinc anode were 43.91% and 73.65%, respectively. The SEM of the exposed sample showed both mud-cracks and pitting corrosion on control, aluminium and zinc anodes protected samples. However, most pitting corrosion were found on the control sample and the aluminium anode protected re-bar sample showed higher pitting than zinc anode protected sample. The higher efficiency of the zinc anode was attributed to its ability to maintain a stable protective oxide layer.

Keywords: Re-bar Corrosion Protection; Sacrificial Anodes; Potentiodynamic Polarization; Marine Environment; Industry; Innovation and Infrastructure (SDG 9)

Introduction

In the field of construction, concrete has established itself as the most widely used material due to its widespread availability, reasonable price, strength, durability, and versatility. This makes it the top choice for civil and infrastructure construction, particularly in marine environments. Steel Reinforced concrete (RC), in particular, is essential in constructing various infrastructures such as buildings, bridges, and marine structures, including piers, docks, and offshore platforms as reported by Shahedan, et al.,2024. However, despite its robust properties, the steel reinforcement is vulnerable to corrosion, particularly when exposed to harsh environments like marine settings (Qu et al., 2021).

Marine environments are characterized by high salinity, moisture, and the presence of aggressive ions such as chlorides and sulphates, which can significantly accelerate the corrosion of the steel reinforcement within concrete. This corrosion process can lead to the deterioration of the concrete, resulting in cracking, spalling, and ultimately, structural failure. Concrete exposed to marine environments is vulnerable to various physical and chemical degradation processes. For example, chemical actions from seawater composition on the hydration products of cement and the crystallization pressure of salts within concrete can cause damage. When the concentration of chloride in reinforced concrete reaches a certain threshold, it accelerates the corrosion rate of steel re-bar. This corrosion, in the presence of sufficient oxygen and moisture, produces expansive pressure, leading to surface cracking, and spalling (Hussain and Ishida, 2010).

In Nigeria alone, industries expend approximately $18.5 million yearly on corrosion-related issues. A 2016 study by NACE International estimated the global cost of corrosion at $2.5 trillion, equating to 3.4% of the global GDP. By implementing effective corrosion control practices, it is estimated that between 15% and 35% of these costs could be saved, amounting to $375 to $875 billion annually as reported by Kosh (2017). Therefore, developing effective methods to protect reinforced concrete from corrosion in marine environments is crucial for ensuring the longevity and safety of these structures.

Corrosion protection of reinforced concrete in marine environments has been extensively researched and developed, with various methods employed to mitigate corrosion. These methods include the use of corrosion-resistant materials, coatings, inhibitors, desalination, electrochemical re-alkalization, electrochemical chloride extraction, and cathodic protection systems (Bertolin et al., 2004; Cardenes et al., 2010; Kupwade-Patil et al., 202; Karthick et al., 2016; Adetunji et al., 2019). Among these methods, cathodic protection, which began being used in concrete around 1955 for submerged and buried structures, has become one of the most effective and standardized techniques. Cathodic protection involves imposing an external voltage on the steel surface to make it cathodic, thereby mitigating corrosion. This approach lowers the corrosion current density by subjecting the steel reinforcement bars to cathodic polarization, achieved by passing a protection current through an external anode to the steel bars as reported by Hasson, 2006. It can be applied through impressed current (active systems) or galvanic or sacrificial anodes (passive systems). Farh et al., 2023 reported that cathodic protection, particularly using sacrificial anodes, has gained significant attention due to its proven ability to stop corrosion, regardless of chloride-ion contamination in concrete.

Sacrificial anode cathodic protection involves attaching a more reactive metal, known as the sacrificial anode, to the steel reinforcement. The sacrificial anode corrodes preferentially, thereby protecting the steel from corrosion. Two commonly used metals for sacrificial anodes in marine environments are aluminium (Al) and zinc (Zn). Both metals have distinct electrochemical properties that make them suitable for use as sacrificial anodes.

Aluminium sacrificial anodes have a high driving voltage, which allows them to provide protection over a larger area. They are lightweight and have a higher current efficiency compared to other anode materials. Zinc sacrificial anodes, on the other hand, have been widely used due to their stable and predictable performance in marine environments. Limited studies exist that compares the protection performances of Al and Zn anodes materials on re-bar in simulated marine environment. Therefore, this study investigated the corrosion protection of steel reinforced concrete by employing Aluminium and Zinc as a sacrificial anode using potentiodynamic polarization method.

Materials and Methods

Sample Preparation

The steel reinforced concrete was prepared using standard procedure with the sacrificial anodes installed into the reinforced concrete except the control sample as shown in Table 1. The steel reinforced concrete specimen was moulded to the desired shape which was cylindrical in nature using PET and was embedded with a 1 cm by 1 cm AISI 1050 mild steel containing 0.53 C, 0.027 Si, 0.622 Mn, 0.119 P, 0.257 S, 0.043 Cr, 0.026 Ni, 0.053 Mo, 0.006 Cu, 0.015 Al, 0.019 V, 0.003 Co, 0.623 Ce and 98.15 Fe, measured in wt.%. Aluminium and zinc based sacrificial anode were employed since they are less noble than steel and will corrode preferentially. A container large enough to accommodate the reinforced concrete specimen and electrolyte solution. It made use of a material that will not react with the electrolyte solution or the concrete, plastic was used. A salt solution of 5 M sodium chloride (NaCl) was used to facilitate the corrosion process, as it was done in Ude et al. (2018) and Adetunji et al. (2016).

S/N	*Code*	*Description*
1	Control	Sample without sacrificial anode
2	Al	Sample with aluminium sacrificial anode
3	Zn	Sample with zinc sacrificial anode

Table 1: Experimental Samples Description.

Potentiodynamic polarization

Small specimens of steel reinforced concrete were prepared for testing, with insertion of respective anode materials before curing in the case of protected samples. Hence, each specimen consisted of concrete with embedded steel reinforcement bars (re-bar) and anode material while the control sample was made of steel reinforced concrete without anode material.

The specimens were mounted in an electrochemical cell, made up of a three-electrode system: a working electrode (the reinforced concrete sample), a reference electrode, and a counter electrode. Electrolyte solution of 5.0 M NaCl was prepared to simulate the corrosive environment which the concrete structure was exposed. Open Circuit Potential (OCP) of reinforced concrete in electrolyte solution was measured until steady state was attained in the rage of ±3 mV. The potential of the working electrode (reinforced concrete sample) was subsequently swept at a controlled rate of 1.0 mV/s in the range of −150 to +800 mV, typically from a more negative to a more positive potential around the OCP. This sweep generated a polarization curve, which shows the relationship between current density and electrode potential.

During the potential sweep, the current passing through the electrochemical cell was measured. This data was used to construct the polarization curve, which provided information about the corrosion kinetics and corrosion potential of the steel reinforcement.

The polarization curve was then interpreted to determine important parameters such as the corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic (βa) and cathodic (β_c) slopes, and polarization resistance (R_p). The corrosion rate for each sample was evaluated according to Equation 1.

$$CR = \frac{K \times E_w \times i_{corr}}{\rho} \qquad (1)$$

where CR is corrosion rate (mm/year), K is a unit conversion constant (3.27×10^{-3} mm.g/ µA/cm/yr), E_w is equivalent weight of steel sample (28.25 g), i_{corr} is corrosion current density (µA/cm^2), ρ is density of material (7.85 g/cm^3).

The protection efficiency was calculated from the evaluated corrosion rate values using Equation (2).

$$P.E. = \frac{CR_{unp} - CR_{pro}}{CR_{unp}} \times 100 \qquad (2)$$

where CR_{unp} is corrosion rate of unprotected sample, CR_{pro} is corrosion rate of protected sample.

Morphology of corroded samples

The surface morphology of the samples were examined by using Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectroscopy (EDS) to evaluate the effects of the sacrificial anodes on the samples and determine the chemical composition of formed corrosion products.

Results

Table 2 shows the chemical composition of the sacrificial anodes used.

While Table 3 has the potentiodynamic polarization data of the rebar in 5M NaCl.

Element/Anode	***Mn***	***Fe***	***Si***	***Cu***	***Al***	***Cd***	***Pb***	***Zn***
Al Anode (wt.%)	0.010	0.080	0.120	0.044	**96.246**	0.0	0.0	3.500
Zn Anode (wt.%)	0.0	0.007	0.123	0.004	3.220	0.120	0.006	**96.520**

Table 2: Percentage Chemical Composition of Sacrificial Anodes.

Potentiodynamic Polarization

Presented in Figures 1-3 are the polarization plots from which data contained in Table 3 were extracted. As seen from these figures, the anodic arms are remarkably different in appearances which indicate changes in the anodic behaviour of reinforcement steel under cathodic protection by Al and Zn anodes. These features of anodic arm in the polarization curves are supported with anodic slope (β_a) values obtained by fitting Tafel on the curves as contained in Table 3 where these values showed increases.

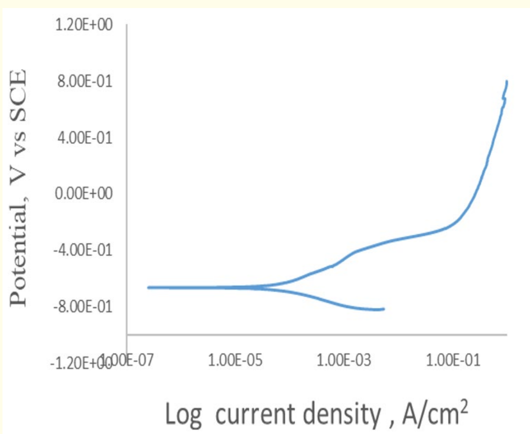

Figure 1: Tafel plot of the control steel sample.

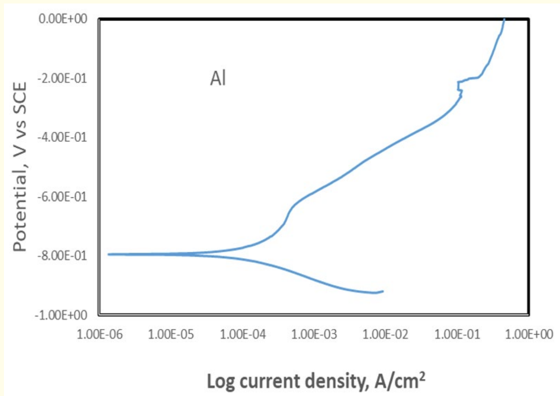

Figure 2: Tafel plot of the Al anode protected steel sample.

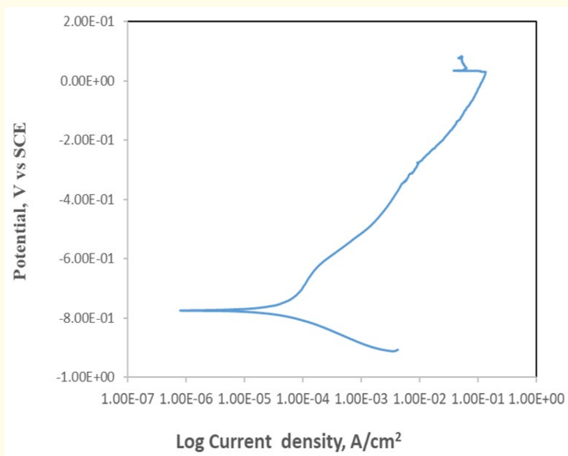

Figure 3: Tafel plot of Zn anode protected steel sample.

Specimen	E_{corr} ***(V)***	i_{corr} ***(μA/cm²)***	β_a ***(mV/s)***	β_c ***(mV/s)***	***CR (mmpy)***	***P.E. (%)***
Control	-6.862	85.1	0.1932	0.1206	1.002	-
Al	-0.775	47.7	0.2266	0.0805	0.562	43.91
Zn	-0.795	22.4	0.4095	0.1290	0.264	73.65

Table 3: Potentiodynamic Polarization Parameters Obtained for The Corrosion of Mild Steel samples in 5M NaCl in the Absence and Presence of Sacrificial Anodes.

SEM Analysis

Surface morphologies of unprotected and sacrificial anode protected re-bar steel samples are presented in Figures 4-6. Pitting corrosion could be observed on all micrographs with the control having most of these (Figure 4), an indication that rebar not subjected to sacrificial anode cathodic protection was more prone to corrosive attack of its environment.

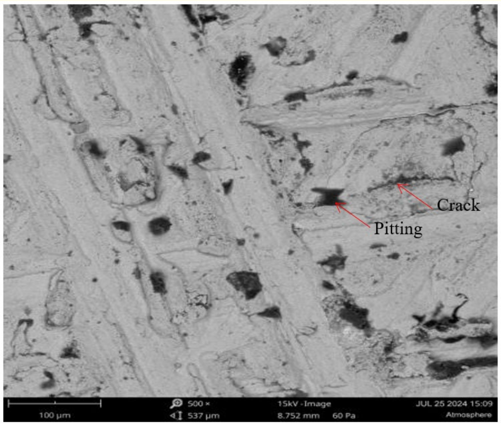

Figure 4: SEM of control.

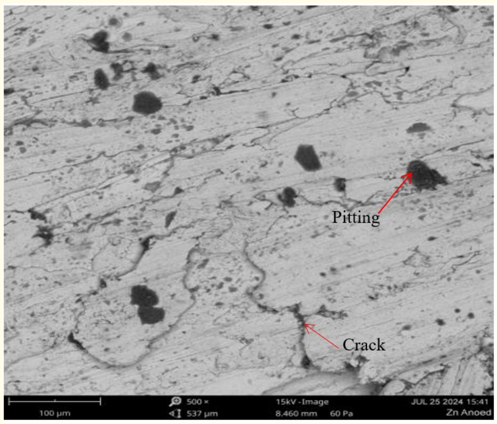

Figure 5: SEM of aluminium protected steel sample.

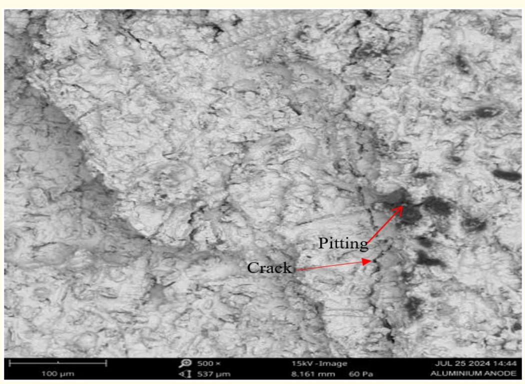

Figure 6: SEM of zinc protected steel sample.

EDS Analysis

Shown in Figures 7-9 are EDS spectra of control re-bar sample, re-bar under Al anode cathodic protection and Zn anode cathodic protection.

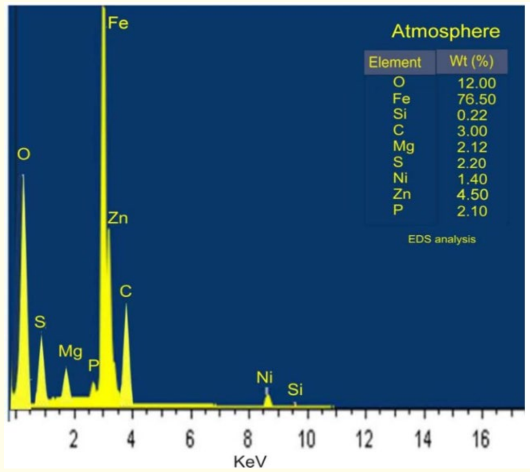

Figure 7: EDS analysis of control sample.

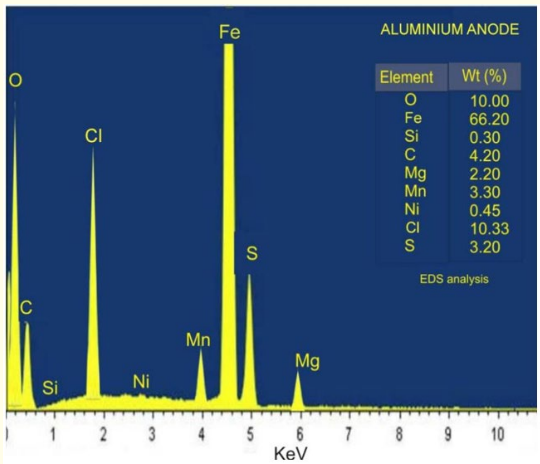

Figure 8: EDS analysis of aluminium anode protected steel sample.

Discussion

The increases in β_a values when re-bar was protected with Al and Zn anodes is a clear indication that anodic reactions on re-bar decreased significantly. On the contrary, the cathodic slope obtained for Al anode protected re-bar showed significant decrease in value and this indicated increase in cathodic reaction on re-bar using Al anode in sacrificial anode cathodic protection of re-bar. Whereas, the cathodic slope recorded Zn anode for cathodic protection of re-bar increased slightly compared to unprotected re-bar sample. Sacrificial anode cathodic protection by Al and Zn anodes on re-bar caused reductions in corrosion current densities from 85.1 μA/

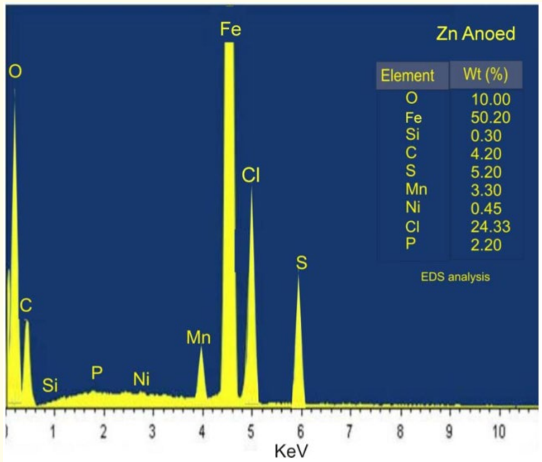

Figure 9: EDS analysis of zinc anode protected steel sample.

cm^2 as obtained for re-bar without cathodic protection, to 47.7 and 22.4 85.1 μA/cm^2 as obtained from re-bar protected with Al and Zn anodes respectively. These lowered corrosion current densities correspond to lowered corrosion rate of re-bar when sacrificial anode cathodic protection using Al and Zn anodes was applied. However, the least corrosion rate was recorded from re-bar protected with Zn anode which recorded a value of 0.264 mmpy. The decreases in corrosion rates resulted in Protection Efficiencies (P.E.) of 43.91 and 73.65% for Al and Zn respectively, with Zn anode providing most efficient form of sacrificial anode cathodic protection against corrosive ions on the concrete re-bar. The decreases in corrosion rates offered by both Al and Zn anodes in sacrificial anode cathodic protection of re-bar corroborates that reported in Owoeye et al. (2020) for sacrificial anode cathodic protection of metal samples in sea water by Al anode. Also, the work of Wang et al., (2020) supports that obtained here where it was found that Zn anode has better protection against steel corrosion in sea water than Al anode. Indication from the polarization plots for Al and Zn anode protected re-bar show formation of passive layer and eventual break in passivity at higher potential, this implies chloride ion ingress which tallied with the report of Wang et al., 2020.

The observed pitting corrosion corroborates reports by Qureshi et al.,2024 that unprotected mild steel structures in marine environment are more prone to destructive failure due to non-formation of passive film on its surface.

However, re-bar subjected to sacrificial anode cathodic protection by Al (Figure 5) tends to possess more of these localized corrosion than that with Zn anode (Figure 6). These ultimately shows that cathodic protection with Zn anode offers better corrosion protection on re-bar than Al anode.

Mud cracks were observed on Al and Zn anodes protected re-bar steel; this was due to chloride ion ingress as it was earlier stated by Prasad et al.,2021 with observation of passive layer break down indicated in polarization curves. Contrarily, these mud cracks are not so prominent on re-bar steel sample without cathodic protection.

Spectrum in Figure 7 for control re-bar sample, shows more percentage of oxygen and iron in the corrosion products than Al and Zn anode protected re-bar in simulated seawater due to highly oxidized iron caused by dissolved oxygen. Reduction of dissolved oxygen in seawater takes place according Equation 3 and water reduction on steel surface takes place in accordance with Equation 4 as reported by Qureshi et al., 2024. These indicate possible formation of $Fe(OH)_2$ as one of the corrosion products due to iron oxidation.

$$O_2 + 2H_2O + 4\,e^- \rightarrow 4OH^- \quad (3)$$

$$H_2O + 2e\text{^-} \rightarrow H_2 + 2OH^- \quad (4)$$

Chlorine spectra detected on re-bar steel protected with Al and Zn anodes confirms the ingress of chloride ions through break down in passivity, leading to mud cracks as seen in the SEM micrographs. Such is caused by chloride ion interacting with compact Fe(OH)2 corrosion product, leading to localized dissolution.

Conclusions

The following conclusions were made from the study evaluating the corrosion protection efficiencies of the use of Aluminium and Zinc anodes in concrete steel reinforcement;

The corrosion rate of the steel sample without anode, was high with a corrosion rate of 1.002 mm/y, followed by the sample protected by the aluminium anode with a corrosion rate of 0.562 mm/y and then the sample protected by the zinc anode had the least corrosion rate with a value of 0.264 mm/y.

The protection efficiency rendered by the aluminium anode was 43.91% while that of the zinc anode was 73.65%.

The SEM image of the exposed steel sample showed uniform corrosion in the control and aluminium protected sample, and the zinc protected sample showed only small number of dark spots, meaning it protected the sample more from corrosion while the Energy Dispersive Spectroscopy plot showed the depletion of iron in the corroded samples.

The study proved that zinc sacrificial anode provides better protection efficiency than aluminium sacrificial anode in the reinforced steel concrete.

Declaration by Authors

There is no conflict of interest between the authors of this research work and all relevant data are contained within.

Acknowledgement

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