

Experimental Studies on the Use of Sacrificial Anode in Oil and Gas Pipeline Corrosion Protection

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Abstract- In this study, Al-Zn-In alloy was used as sacrificial anode to protect an oil and gas transportation pipeline in seawater environment. Laboratory testing of the sacrificial anode was done to evaluate its electrochemical capacities at various current densities: 1.5A/cm², 0.4A/cm², 4.0A/cm², 1.5A/cm² for 4 days (96 hours). Design problem was also solved and it was discovered that 155 anodes would be required to protect a pipe of diameter 0.152m and length 20km in the environment.

Keywords: Sacrificial anode; electrochemical; pipeline; current density; corrosion

1. INTRODUCTION

Petroleum products transportation is commonly achieved through pipeline systems which are fabricated from low carbon steels or galvanized steels. Naturally, steels have the tendency to revert to its original form (that is iron-oxide) when in contact with moist or wet environment. This reversal of steel to its native form otherwise known as corrosion often has consequences such as loss of strength which jeopardize the integrity of the pipeline structure [1]. Corrosion in a broad sense is the degradation or deterioration of material due to reaction with the environment. It occurs in virtually all materials but mostly associated with metals.

Amongst the prevailing factors affecting corrosion of buried pipelines is soil environment are soil type, ground water, soil PH and soil resistivity. Obviously, some soil types are more corrosive than others. The origin of soils, along with climate, geology location, plant and animal life, and the effects of man, all influence soils corrosion potentials [2]. Extremely acidic soils (below PH 4.5) and very strongly alkaline soils (above PH 9.1) have significantly high corrosion loss rate in comparison to other soils. Likewise, soil resistivity or reciprocal of conductivity is the one variable that has the greatest influence on

corrosion rate. In general, the lower the moisture contents of a soil, the higher the soil resistivity to corrosion [2]. For instance, sandy soils which drains water away easily are typically noncorrosive whereas, clay soils that are water tight have low resistivity, thus are corrosive.

In a nutshell, there is no mystery about corrosion; it is an environmental phenomenon that obeys the laws of nature. Hence, one way to reduce the corrosion rate is to lower the corrosion potential in the immune region and this could be clearly observed in the poubaix diagram for carbon steel in water with PH7. Also, lowering the corrosion potential will reduce the current density on the anodic reaction (iron dissolution), consequently this is called cathodic protection (CD) which is achieved by supplying an external current to the structure to be protected. Moreover, to cathodically protect pipelines, two systems are employed: the impressed current systems which are applicable where electric power is available, especially where current requirements are large or soil resistivity is relatively high, and the galvanic (sacrificial) anode system which uses more electrochemically active metals (aluminum, zinc and magnesium).

According to Nigeria National Petroleum Corporation (NNPC) quarterly magazine, pipeline operations

worldwide spend millions of dollars annually in pipeline inspections, evacuating sites, repairs and replacing damaged sections of the pipe due to internal and external corrosion [1]. However, alternative corrosion prevention mechanism is coatings, but there are always flaws in it when metal is in contact with the surrounding soil or water or corrosive environment, cathodic prevention is therefore used to preventing corrosion at these coating flaws [3].

The propulsion for this research work evolved as the Petroleum Products Marketing Company (PPMC), a subsidiary of Nigeria National Petroleum Corporation (NNPC) intended to cathodically protect a pipeline transporting petroleum products from Warri deport to Lagos deport in Nigeria through the sea. The pipeline was to be protected using bracelet sacrificial anodes, hence the thrust of this study to design an effective Al-In-Zn alloy system for protecting the facility.

Table 1: Anode Mould Design Parameters

Insert for reinforcement	Anode					
	Radius (mm)		Thickness (mm)	Weight (kg)		Length (mm)
	Internal	External		Net	Gross	
2.5kg	76	14	38	20	22.5	100

Table 2: Alloy Composition for the Sacrificial Anode

Composition %	Element							
	Fe	Si	In	Zn	Cu	Other (each)	Other (ToT)	Al
Min %	0	0	0.015	4.75	0	0	0	Balance
Max %	0.08	0.12	0.02	5.75	0.003	0.02	0.05	-

2. EXPERIMENTAL METHODOLOGY

The mould was fabricated using predefined geometry and size dimensions of the bracelet anode to be produced as given in table 1. The steps involved acquiring and sectioning the mild steel of choice, preparing alongside assembling of the two blocks for drilling and boring to get the required size, then aligning the blocks in order to fasten them using belts.

The Al-Zn-In alloy was charged into the furnace using the mass ratio of Al:Zn:In to 100:50:0.18. Consequently, the production of bracelet anode of net weight of 30kg, the alloy mass ratio of Al:Zn:In which gives (28.6:1.4:0.00017) kg, in other words, 28.6kg of Aluminum, 1.4kg of Zinc and 0.00017kg of Indium was

charged into the furnace for casting. The molten metal was then poured into the predefined mould and continuous spraying of water was used as the cooling medium. The cast metal was machined to smooth the surface and thereafter, the surface of the anode facing the object to be protected was coated to avoid corrosion in that part of the structure. Cable connections made of steel and copper was set up which passes current from the anode and cathode to the protected structure. The steel cable was connected to anode while the copper cable was connected to the cathode. In order to determine the electrochemical capacity of the bracelet anode, which was measured in ampere hour per kilogram (Ah/kg), a cylindrical test specimen with 10mm diameter and 50mm length was prepared. A hole of 2mm diameter was drilled and tapped at one end for connection

of Titanium support rod. The specimen was then rinsed in tap water followed by ethanol, dried and weighed.

After mounting the specimen ends and the support rod successfully, the part of the rod exposed to the test solution was coated using polychloroprene glue. The corrosion test solution used was neutral seawater of adequate purity and salinity (30% minimum). The specimen was suspended at the center of uncoated cylindrical steel container (made of a pipe section), the wet surface area of which was a minimum of 20 times the exposed anode specimen area, approximately 400cm² minimum.

Galvanostatic control was influenced by means of a DC constant current source capable of controlling the current. The specimen and the cathode were coupled to the positive and negative rectifier terminals respectively. Current flowing through the cells was adjusted to provide anodic current densities based on their initially exposed surface area in accordance with the following scheme: Day 1[1.5mA/cm²], Day 2[0.4mA/cm²], Day 3[4.0mA/cm²] and

Day 4[1.5mA/cm²]. Furthermore, the current density was controlled to an accuracy of 0.1mA/cm² and was maintained for a period of 24hours. At the end of each testing period, the anode potential was measured at three different positions per specimen using a standard reference electrode (Ag/AgCl) with an electrolyte bridge.

3. RESULTS AND DISCUSSION

In determining the electrochemical capacity, weight loss and Current density alongside the numerical strength of anodes capable of protecting 6'' 20km pipeline exposed in sea water were measured. The followings results were recorded and analyzed statistically including the design deductions.

Table 3: Electrochemical capacity, weight loss and Current density

Duration of experiment	Electrochemical Capacity, $\epsilon = (Cx100)/\Delta w$ (Ah/Kg)	Weight of Sample (g)		Weight Loss (m1-m2) Δw (g)	Current density (mA/cm ²)	Circuit Potential (mV)	
		Initial (m1)	Final (2)			open	closed
Day 1 24hrs	2609	11.50	10.43	1.07	1.5	-1107	-1099
Day 2 48 hrs	2659	10.43	9.38	1.05	0.4	1113	1109
Day 3 72 hrs	2561	9.38	8.29	1.09	4.0	-1108	-1099
Day 4 96 hrs	2634	8.29	7.23	1.06	1.5	-1123	-1108

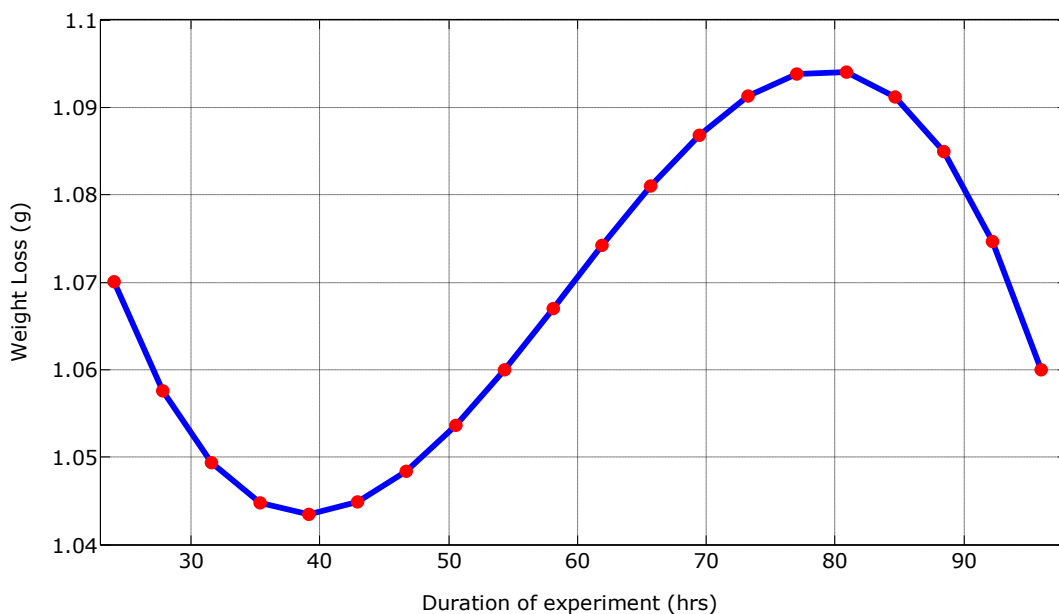


Figure 3: The variations of weight loss in sacrificial anode with time.

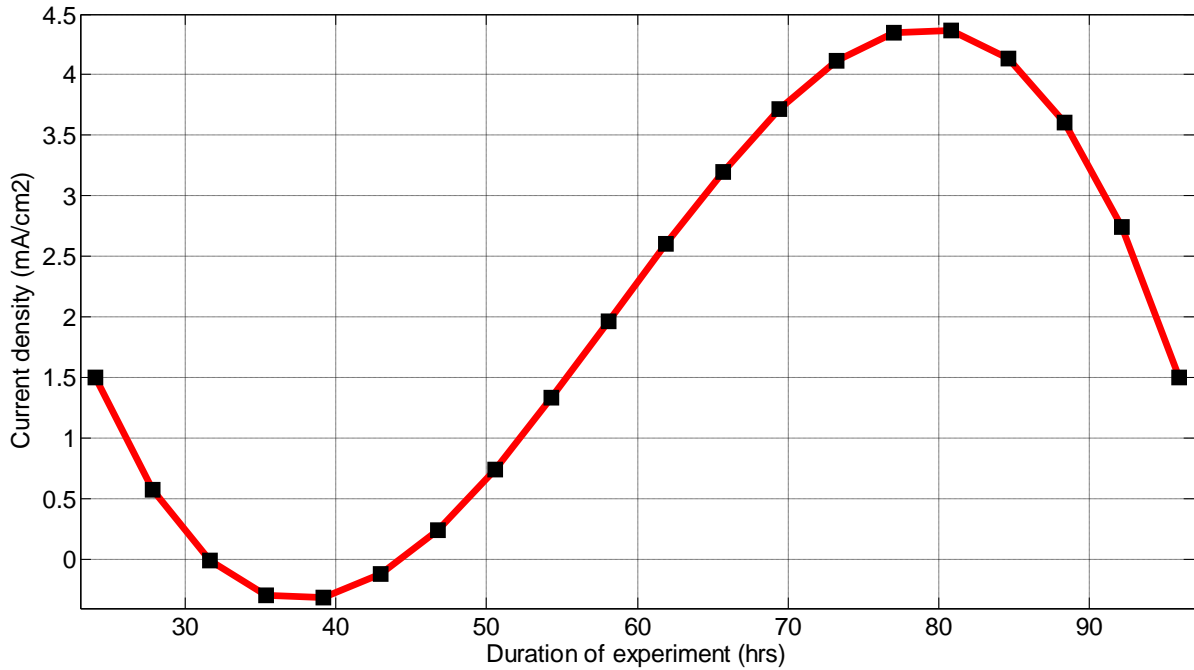


Figure 4: The variations of current density in sacrificial anode with time.

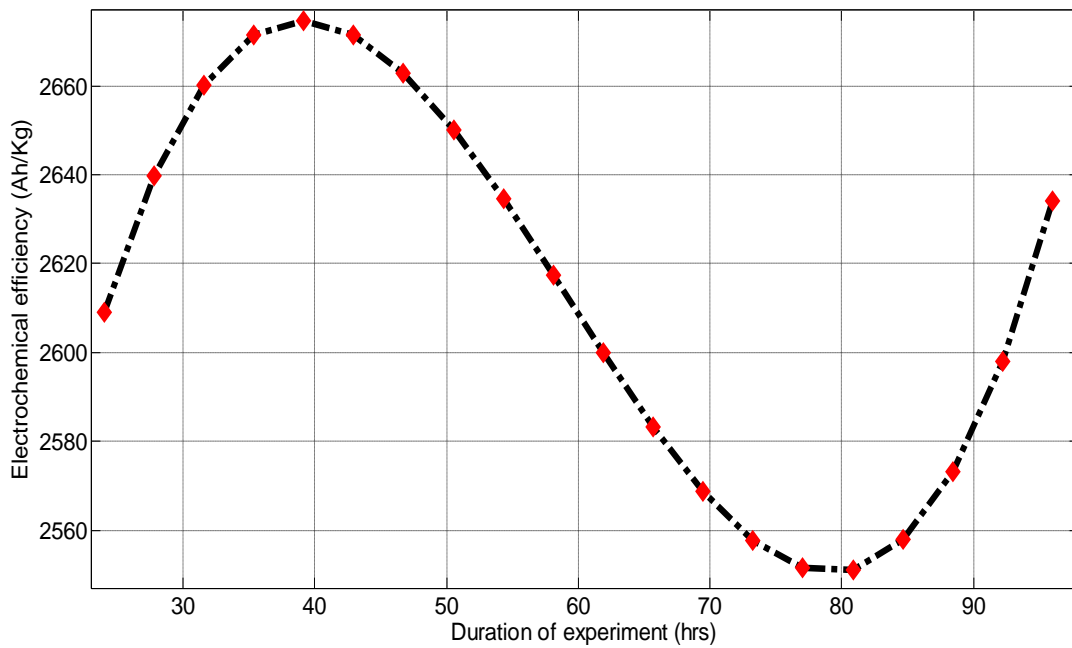


Figure 5: The variations of Electrochemical Efficiency in sacrificial anode with time

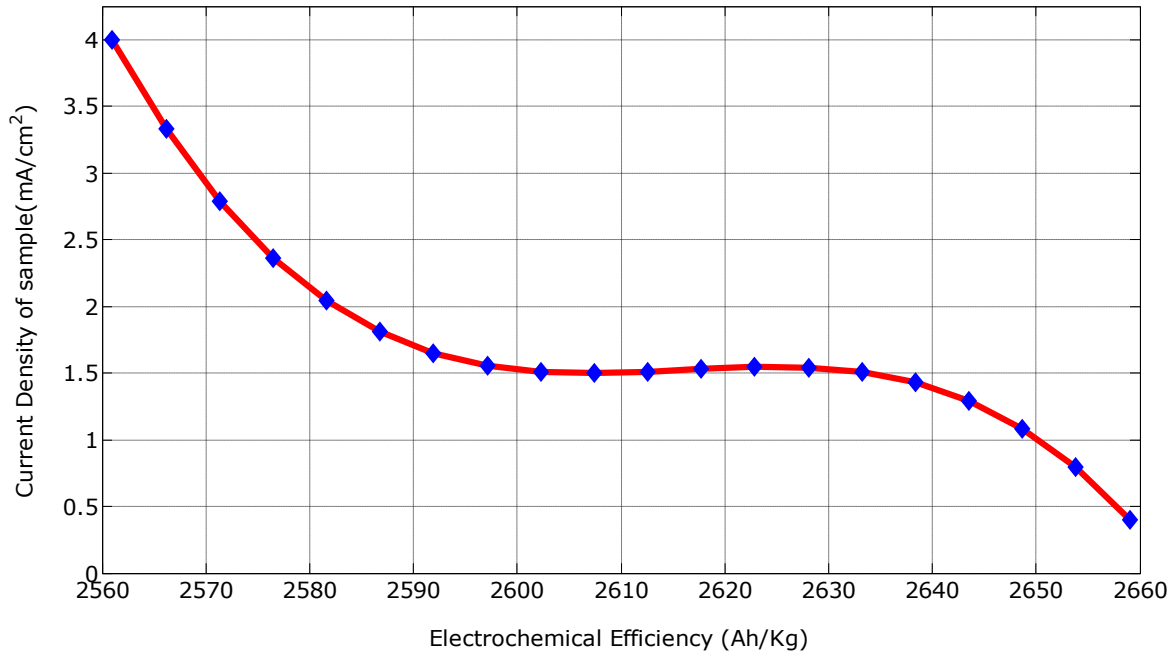


Figure 6: The variations of Current Density with Electrochemical Efficiency in sacrificial anode

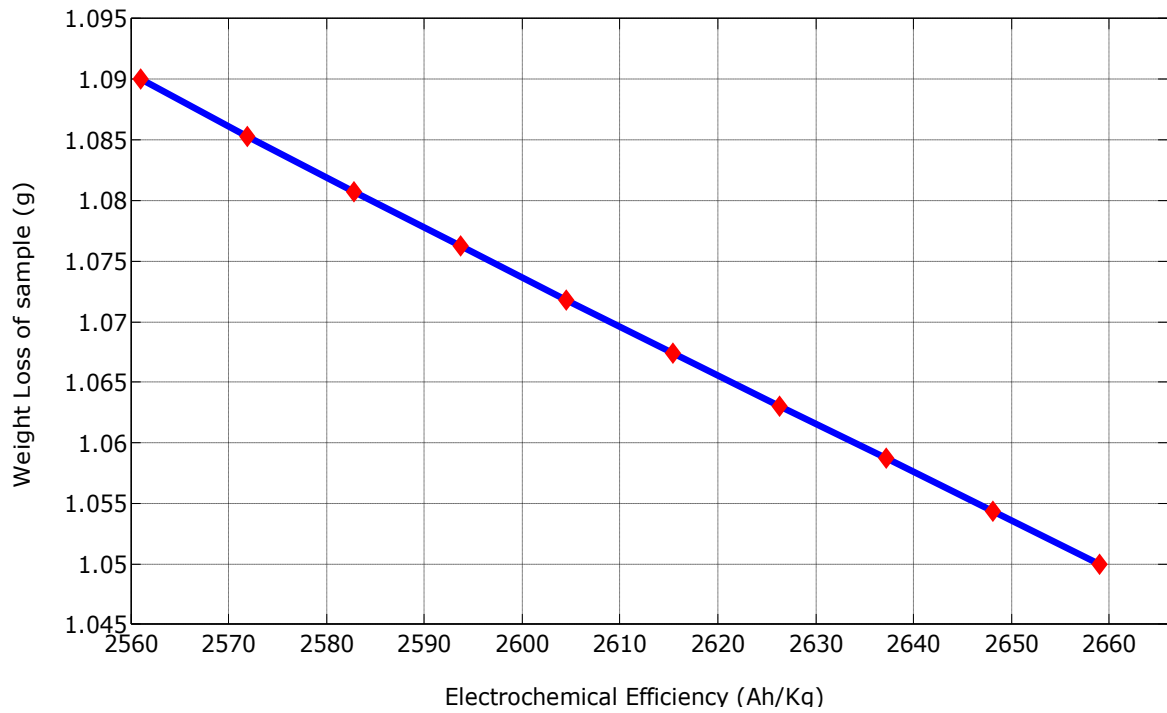


Figure 7: The variations of Weight Loss with Electrochemical Efficiency in sacrificial anode.

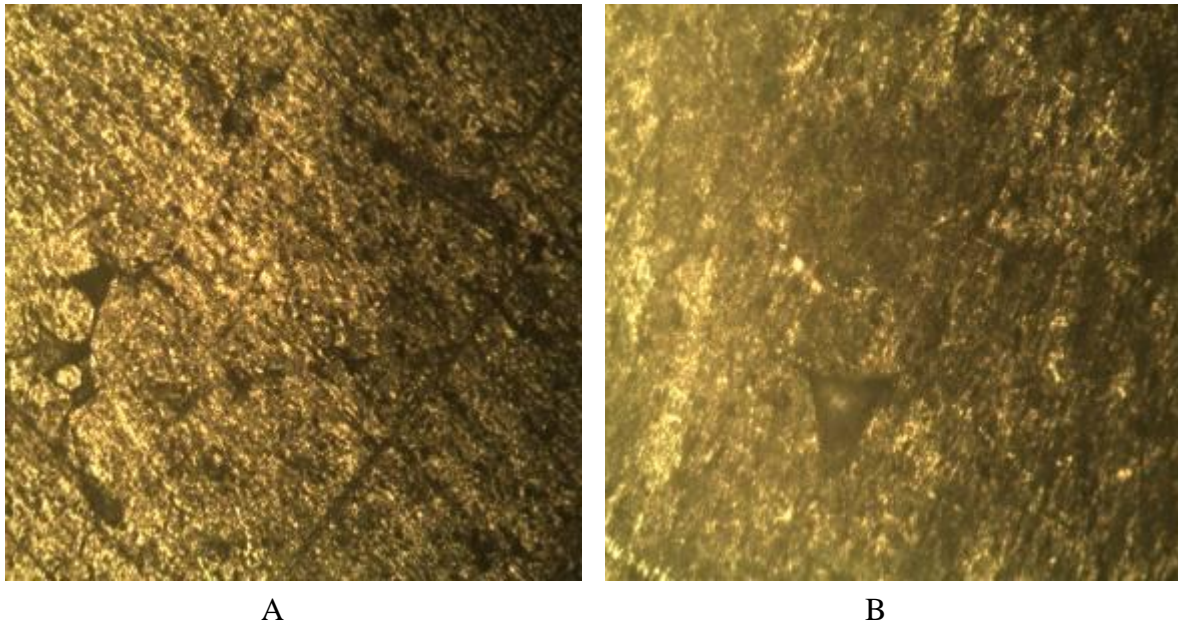


Figure 8: Micrograph of the anode: (A) before corrosion and (B) after corrosion

From the graph in Figure 3, the weight loss has similar characteristics as current density with a slight different. The values at the beginning and the end are not the same as that of current density even though the same barrier that affected weight loss is a function of current density.

On the result of the figure 4, it can be seen that the current density make a sinusoidal line graph which depict that the current density at the beginning and the end of the experiment (Day 1 and Day 4) happened to be the same. After some hours of exposure of the sample to artificial agitation on the exposed surface of the material, the protective film formed was destroyed or deteriorated. As the experiment proceeded, the current density started building up again, which started no sooner will cease supply forced air that caused the agitation up to the 80th hour. The study of current density vis-a-vis the sacrificial anode is actually to understand the effect of agitation (ocean current) on passivity. The sample was exposed to artificial agitation for the first 40th hours thereafter ceased for the next 40 hours and then continues with the application of artificial agitation for the rest of the experiment.

Conversely, electrochemical capacity of the sample under study exhibit direct opposite features when compared to weight loss and current density of the sample as can be noticed from Figure 5. When the material was artificially agitated from the first hour to the 40th hours of the experiment, the electrochemical capacity is on the increase in other words, artificial agitation encourages electrochemical capacity.

Figure 6 has a quasi-look like that of weight loss and that of current density plotted against duration of the experiment. It is apparent as the electrochemical capacity increases the current density decreases from the first hour of the experiment. At Electrochemical capacity values of 2600 and 2620Ah/kg it can be inferred that the current density of the sample consolidate. Nevertheless passivity set in between the range, when the current density was approximately 2600Ah/kg through 2630Ah/kg before the application of artificial agitation which hamper current density and also started decreasing till the end of the experiment. Furthermore the variation of weight loss of the sample with electrochemical capacity agrees that weight loss is a function of current density.

The experimental results obtained have shown that as the electrochemical capacity of the anode increases, there is resultant decrease in the weight loss of the anode which also agreed with the graphical interpretation contained in Figure 7. Consequently upon this, it should be expected that the weight loss of the anode is inversely proportional to the electrochemical capacity of the anode. It is also evident from the results of electrochemical capacity examination that at various current densities, the electrochemical capacity observed would be higher than the standard value of 2500Ah/Kg. Hence, the standard value can be used for the cathodic protection design for pipelines used in the environment under consideration. It is obvious that weight loss has a negative linear relationship with electrochemical capacity of the sample as the weight loss started decreasing from the hours through last hours forming a straight jacketed line. In other words, weight loss

of the specimen varied inversely proportional to electrochemical capacity of the material. Furthermore, it can be deduced from the micrograph in figures 8a and 8b that the protective film on the metal surface which provides passivation in figure 8a was progressively leached thereby exposing the metal surface to further corrosion attack in figure 8b. In addition, the micrograph of the anode sample before and after corrosion reveals that the grain structure had been affected as a result of corrosion. Figure 8a shows that all the components of the alloy are still present, meaning that corrosion has not occurred, but in contrast, figure 8b depicts that one of the component alloy has been selectively removed and this component removed is Zinc, which make the micrograph look dull. The process of selective removal of zinc from zinc containing alloy is called dezincification. This actually affects the mechanical property of the anode.

Table 4: Cathodic Protection Design Criteria

INPUT DATA	DESCRIPTION	REFERENCES
Design life	20 years	Section 2.5 of Kita Basis of Design
Sea water temperature (max)	29°C	Section 2.6 of Kita Basis of Design
Sea water temperature (min)	24°C	Section 2.6 of Kita Basis of Design
Seabed temperature (max)	28°C	Section 2.6 of Kita Basis of Design
Seabed temperature (min)	15°C	Section 2.6 of Kita Basis of Design
Max storm wave height(1 year)	5 m	Section 2.6 of Kita Basis of Design
Resistivity of Sea water	33.9 Ω.cm	Adanga sea water analysis (10 & 20ft)subsurface by Corelab Nigeria Limited
Anode Utilization factor, U	0.80	Table 10-8 of DNV-RP-B401
Protective Potential(E°_c)	-0.80 V	Section 5.4 of DNV-RP-B401
Close circuit potential for anode in sea water (E°_a)	-1.05 V	Table 10-6 of DNV-RP-B401
Driving potential ($E^{\circ}_c - E^{\circ}_a$) in sea water	0.25 V	Section 7.8.2 of DNV-RP-B401
Electrochemical capacity of anode in sea water(ϵ)	2500 (Ah/Kg)	Table 4 of ISO 15589-2-2004R
Current density for seawater, mean	70 mA/m ²	As Per Addax Specification IFU-00-6-SPC-005
Current density for seawater, final	90 mA/m ²	As Per Addax Specification IFU-00-6-SPC-005
Current density for seamud (initial, mean & final)	20 mA/m ²	Section 6.92 of DNV-RP-B401
Mean Coating breakdown factor (f_m) for risers in splash zone	5%	As Per Addax Specification IFU-00-6-SPC-005
Final Coating breakdown factor (f_f) for riser in splash zone	7%	As Per Addax Specification IFU-00-6-SPC-005
Mean Coating breakdown factor (f_m) for pipeline in submerged zone	5%	As Per Addax Specification IFU-00-6-SPC-005
Final Coating breakdown factor (f_f) for pipeline in submerged zone	7%	As Per Addax Specification IFU-00-6-SPC-005

International codes and standards implemented in this work are as contained in table 4. The cathodic protection system design for the pipeline steel structure is in accordance with the endorsement of NACE-RP-0176 and DNV-RP-B401. The bracelet anode selection of Al-Zn-In is in line with DNV-RP-B401

3.1 Pipeline Parameters:

Length and diameter = 20km and 6inches respectively,
 Bracelet internal diameter = 152 mm

Anode Length (La) = 100 mm, Anode thickness (ta) = 38 mm, Gap between two half-shell anodes (Ga) = 51 mm, Anode Weight = 20Kg and Thickness of Coating (te) = 2.9 mm

3.2 Calculation Details

Area of the pipeline $A = \pi DL$

Eq (i)

Where, D= diameter, L= length of the pipeline
 D= 6inches= (6*25.4) mm = 152.4mm = 0.152m, L = 20km = (20*1000) m = 20,000 m
 $A = \pi * 0.1524 * 20000 = 9575.57m^2 = 9575.57m^2$

$I_{requirement} (mean) current = i_m X f_m X A$

Eq(ii)

Where: i_m = mean current density = 70mA/m²
 f_m = mean coating breakdown factor = 5% = 0.05
 $I_m = (70/1000) A/m^2 * 5% * 9575.57m^2 = 33.51A$

$I_{requirement} (final) = i_f X f_f X A$

Eq(iii)

Where: i_f = final current density = 90mA/m²
 f_f = final coating breakdown factor = 7% = 0.07
 $I_f = (90/1000) A/m^2 * 7% * 9575.57 m^2 = 60.33 A$

3.3 Quantity of Anodes by weight method (N_{am}):

$N_{am} = M/m_a$

Eq(iv)

Where: M = Total weight of the anode required throughout the design life of structure.

m_a = weight of a single anode = 20kg

$M = I_{t\ mean} * design\ life * 8760 / (u * \epsilon)$

Eq(v)

Where: $I_{t\ mean}$ = total mean current = 33.51A

Design life = 20years

U = utilization factor = 80%

ϵ = Electrochemical capacity = 2500Ah/Kg

$M = (33.51 * 20 * 8760) / 0.80 * 2500 = 2935.48\ kg$

$N_{am} = 2935.48 / 20 = 146.77 = 147\ anodes$

3.4 Quantity of Anodes by final current (N_{af})

$N_{af} = \frac{I_f}{I_{af}}$

Eq(vi)

Where: I_f = Total final current delivered by the anodes.

I_{af} = Current delivered by an anode using total initial current

$I_{af} = \frac{E}{R_{af}}$

Eq(vii)

Where : E = Driving potential = $E_c - E_a$

E_c = protective potential = -0.80V

E_a = anodic potential = -1.05V

$E = -0.8 - (-1.05) = 0.25V.$

R_{af} = Resistance of anode = $(0.315 * \rho) / \sqrt{A\ final}$

Eq(viii)

Where: ρ = Resistivity of the sea water = 33.9 Ω

A = Area of the Anode

$A_{(Final)} = \pi * (D + 2 * (t_e + (1-u) t_a)) * La - 2 * Ga * La$

Eq(ix)

Where: D= Diameter of the anode = 0.1524m

t_e = thickness of the coating = 2.9mm = 0.0029m

u = utilization factor = 80% = 0.80

t_a = thickness of the anode = 38mm =

La = length of the anode = 100mm = 0.10m

G_a = gap between the two halves of the bracelet anode = 51mm = 0.051m

Therefore,

$$A_{(Final)} = \pi * (0.1524 + 2(0.0029 + (1 - 0.8) * 0.038) * 0.1 - 2 * 0.051 * 0.1) \\ = 0.48538 - 0.0102 = \underline{0.475m^2}$$

Substituting into equation (viii)

$$R_{af} = \underline{0.155 \Omega}$$

$$I_{af} = \frac{E}{R_{af}} = 0.25 \text{ V} / 0.155 \Omega = \underline{1.61 \text{ A}}$$

$$N_{af} = \frac{I_{f(final)}}{I_{af}} = 60.33 / 1.61 = 37.4 = \underline{38 \text{ anodes}}$$

3.5 Determination of Anode Quantity (Q_{pipeline})

The larger of N_{am} , N_{af} , is Chosen as (Q_{pipeline}) = 147 anodes

Considered an additional contingency factor = 5 %

Total number of anodes = $8 + 147 = \underline{155 \text{ anodes}}$

3.6 Checking of anode Quantity (Q_{pipwlinw})

The following equations below were used to check for the correctness of the number of anodes recommended initially in accordance with section 7.8.4 of DNV B401 Cathodic Protection.

$$\bullet N * Ca \geq I_{\text{total mean current}} * \text{design life } (t_f) * 8760$$

Where Ca is the individual anode current capacity (A .h) = $ma * u * \epsilon$

$$\bullet N * I_{af} \geq I_{t(final)}$$

3.7 Confirmation Calculations

$$\bullet N * Ca \geq I_{\text{total mean current}} * \text{design life } (t_f) * 8760$$

$$155 * 20 * 0.8 * 2500 \geq 33.51 * 20 * 8760$$

$$6,200,000 \geq 5,870,952$$

$$\bullet N * I_{af} \geq I_{t(final)}$$

$$155 * 1.61 \geq 60.330, \text{ this implies that } 247.5 \geq 60.33$$

The aforementioned confirmations are evidence that, the recommended number of anodes of 155 and 165 for 6” 20 km pipelines can effectively mitigate the corrosion of the pipelines throughout the expected life of the structure.

4. CONCLUSION

The results from this study confirmed that:

1. The electrochemical capacities evaluated are higher than the standard value of 2500Ah/Kg. This is necessary as the electrochemical capacity varies with the environment and if the value evaluated from the test is lower than the standard value, then it is not safe to base cathodic protection design on the standard value.
2. Therefore values lower than the standard value should always be chosen.
3. Also, it is evident that those 155 anodes evaluated can effectively protect the 6” 20km pipeline throughout its design life.

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