Studies on Cathodic Protection of Steel Materials in Seawater

Emmanuel J. Ekott, Ubong I. Etukudo

Abstract— **Several process industries transport commodities through long distances within steel pipes. In most cases the routed pipes are exposed to different electrolytic environments with varied tendency to cause corrosion. In aqueous electrolytes corrosion is intensified by high salinity, the presence of carbon dioxide, hydrogen sulfide, and oxygen. In this study the corrosion rates of cathodically protected and un-protected steel materials immersed in high saline electrolyte medium was studied. Impressed current from a 12 volt DC power source was employed for cathodic protection in sea water of salinity 32.47 ppt. Weight loss method was used at the interval of seven days to ascertain the corrosion rates in this medium. High corrosion rate was recorded for un-protected steel compared to the loss for cathodically protected. A total of 0.15g (2.5%) and 0.32g (5.33%) was lost by the protected and un-protected steel materials respectively. This result implies that in sea water the corrosion of steel materials can be controlled since 53% protection was achieved for steel material using cathodic protection method in this study.**

*Index Terms*— **Electrolytic environment, saline medium, cathodic protection, steel pipe.**

I. INTRODUCTION

Several industrial equipment and pipes are operated in sea with high corrosive saline environments for transportation and storage of crude oil, natural gas and other petroleum products. Sea water contains great amount of inorganic salts, mostly chloride, and has high conductivity; hence these saline environments enhance corrosion of steel structures thereby increase operational and maintenance costs. Cathodic protection can be effectively applied to mitigate saline water corrosion. Achebe, Nneke and Anisiji (2012) identified causes of pipeline failures in Niger Delta of Nigeria to include aging, mechanical failure and corrosion. They maintained that corrosion accounted for 18% of pipeline failure. Several adverse effects are associated with pipeline failures; it results to high degree of environmental, human and economic consequences (Okoroafor, 2004).

Okah-Avae (1996) stated that the corrosion protection of marine equipments and offshore structure is achieved by sacrificial anodes or impressed current cathodic protection systems as shown in figure 1. Structures commonly protected are the exterior surfaces of pipelines, ships' hulls, jetties, foundation piling, steel sheet-piling and offshore platforms as

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well as interior surfaces of water-storage tanks and water-circulating systems. Cathodic protection has also been applied to steel embedded in concrete, to copper-based alloys in water systems, and, exceptionally, to lead-sheathed cables and to aluminum alloys, where cathodic potentials have to be very carefully controlled. Veritas (2011) noted that cathodic protection has the faults of hydrogen related cracking of certain high-strength alloys and coating disruption.

In aqueous electrolytes, corrosion of steel is an electrochemical process in which anodic and cathodic electrochemical reactions occur simultaneously. In such instance the corrosion rates of both anodic and cathodic reactions are equal hence; no net overall charge builds up on the metal surface. On the steel surface anodic reactions involves oxidation of iron to iron ion with the release of electrons thus:

$$2Fe \rightarrow 2Fe^{2+} + 4e^- \qquad [1]$$
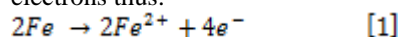
Conversely, the cathodic reaction involves reduction of water molecules and dissolved oxygen to yield hydroxyl ions which bonds with iron ion to form an alkali.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad [2]$$
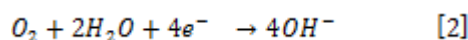
These reactions are observed on steel surfaces. Corrosion detection, monitoring and control are important factors considered when maximum equipment life span, minimum cost and maximum safety are considered.

Ekott, Akpabio and Etukudo (2013) stated that cathodic protection set-up involves the application of appropriate direct current from an external source to the surface of steel in contact with electrolyte to oppose the discharge of corrosion current from anodic areas. When this protection system is installed, all exposed portions of the protected steel surface become a single cathodic area. Sacrificial anode and impressed current are the two methods used to achieve this protection.

Unlike the impressed current system, sacrificial anode technique requires no external rectifier for direct current supply. Materials chosen for sacrificial anodes are usually less noble in the galvanic series than those to be protected. For example, aluminum, magnesium and zinc are sacrificial anodes of choice for the protection of steel structures. While zinc is used most in low resistivity soil and water, aluminum is preferred for saline water due to its high energy capacity per anode weigh (Ekott *et al*, 2013).

In impressed current protection a direct current supplied by an external rectifier passes through an anode before reaching the protected metal surface. The standard electromotive force

(EMF) of metals is presented in table 2. From the table, aluminum and zinc are of greater negative electrode potential than iron or steel hence, they are used as anodes for steel in impressed current protection. Okah-Avae (1996) described that impressed current technique is a more applicable approach for combating corrosion of metals immersed in corrosive electrolytes.

In water, immersed steel material receives direct current (DC) from a power source through aluminum or zinc (electrode) placed some distance away from the steel. The steel becomes the cathode and the electrode the anode. The anode which is a less noble metal than steel in the standard EMF series has higher corrosion rate hence requires continual replacement. Over 90% protection was achieved from previous studies conducted by Ekott *et al,* (2012 and 2013) on cathodic protection using swampy and loamy soil as electrolyte.

II. MATERIALS AND METHODS

Saline water sample from Atlantic Ocean shore of Niger Delta, Qua Iboe Termina, Ibeno, Akwa Ibom State Nigeria was collected. The saline water was filled in two plastic vessels measuring 20, 000 cm^3 each. Two steel rods measuring 50cm in length and 2.75mm in diameter, and a zinc sheet measuring 5cm by 15 cm ($75cm^3$) were obtained from a commercial shop in Eket, Nigeria. A 12 volt DC rectifier and a 12 voltage accumulator were used to produce the impressed current for the experiment while an electronic weighting balance (model: D – 46397) was used for all weight measurements.

With the aid of a thin core copper wire, one of the steel rods was connected to the negative terminal of the DC source, while the zinc anode was connected to the positive terminal of the power source. The copper (cathode) and zinc (anode) were immersed in the saline water and the rectifier connected to the A.C mains and switched on as shown in figure 1.

After every seven days the metals were removed from the water and detached from the circuit. They were rinsed with tap water, oven dried for one hour at 100^oC (to eliminate absorbed water molecules), weighted and the circuit re-installed before re-immersion into the saline water and powered. The weight losses of the metal samples were noted over a period of 70 days.

The salinity of the water electrolyte was determined using gravimetric precipitation method developed by Skoog, West, Holler and Crouch (2009). Drops of 1.0 M silver nitrate ($AgNO_3$) solution were added to 100 ml of the water sample for complete formation of silver chloride (AgCl) precipitate as shown in equation 3. The solution was kept for 24 hours for completeness of reaction. The resultant solute was recovered by decantation and oven dried for analysis.
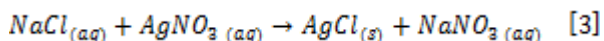
$$NaCl_{(aq)} + AgNO_{3\,(aq)} \rightarrow AgCl_{(s)} + NaNO_{3\,(aq)} \quad [3]$$

Figure1: Schematic of Impressed Current Cathodic Protection systems.
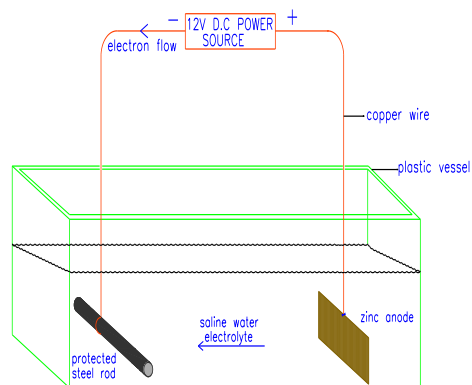
Table1: Weight loss of materials

Number of days	Weight loss for un-protected steel		Weight loss for protected Steel	
	Gram	%	gram	%
7	0.14	2.33	0.02	0.33
14	0.18	3.00	0.03	0.50
21	0.20	3.33	0.05	0.83
28	0.25	4.18	0.06	1.00
35	0.25	4.18	0.07	1.17
42	0.29	4.83	0.10	1.67
49	0.30	5.00	0.11	1.83
56	0.32	5.33	0.13	2.17
63	0.32	5.33	0.15	2.50
70	0.32	5.33	0.15	2.50

III. RESULTS AND DISCUSSION

Table 1 shows the result for the experiment at the end of 70 days. The cathodically protected steel had negligible weight loss after every seven days compared to weigh loss rate for un-protected steel. It was observed that the un-protected and protected steel samples showed no further weight loss after forty nine (49) and fifty six (56) days respectively. At the end of ten (70) days of the experiment, the weight loss recorded for un-protected steel 0.32g (5.33%) was slightly more than twice the amount lost by the protected steel 0.15g (2.50%).

In similar studies conducted by Ekott, Akpabio and Etukudo (2012) and (2013), loamy and swampy soil samples serves as electrolytes for the impressed current circuit. 96% and 90% protection were obtained for the protected steel material. However, only 53% protection is obtained in this study with saline sea water as electrolyte. The higher corrosion rate recorded with saline water as electrolyte is probably due to the high electrolytic environment which enhances corrosion.

IV. CONCLUSION

In this study, the protected steel lost only 2.50% of its original weight against 5.33% lost by the unprotected steel, with 53% protection achieved for the protected steel. Comparing this result with previous studies, 96% and 90% protection was obtained for protected steel in loamy and swampy soil as electrolytes. This shows that the corrosion rate of steel is high

in medium with high moisture and ion contents. It seems that the more aqueous the medium, the more the rate of corrosion.

The protection achieved in this study has showed that corrosion of steel material in saline sea water can be controlled with appropriate amount of impressed electric current and the right sacrificial anode in place. Further studies should be carried out to improve the protection obtained by determining the salinity of the electrolytic medium and then a relationship between salinity level, protection voltage, and corrosion rate should be investigated
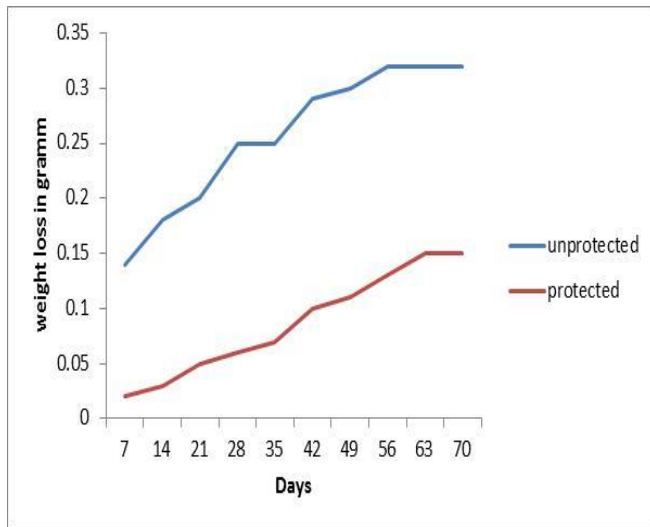

Figure 2: Variation of weight loss with exposure time for the metal samples.

Table 2: Standard EMF Table (Adapted from Total Manual)

Status	Metal name	Metal-Metal equilibrium (unit activity)	Electrode potential (in volts) vs. normal hydrogen Electrode at 25oC
Active or anodic	Potassium	$K - k^+$	$- 2.925V$
	Sodium	$Na - Na^+$	$- 2.714V$
	Magnesium	$Mg - Mg^{2+}$	$- 2.363V$
	Aluminum	$Al - Al^{3+}$	$- 1.562V$
	Zinc	$Zn - Zn^{2+}$	$- 0.763V$
	Chromium	$Cr - Cr^{3+}$	$- 0.744V$
	Iron	$Fe - Fe^{2+}$	$- 0.440V$
	Cadmium	$Cd - Cd^{2+}$	$- 0.403V$
	Cobalt	$Co - Co^{2+}$	$- \quad 0.277V$
	Nickel	$Ni - Ni^{2+}$	$- 0.250V$
	Tin	$Sn - Sn^{2+}$	$- 0.136V$
	Lead	$Pb - Pb^{2+}$	$- 0.126V$
	Hydrogen	$H - H^+$	0
	Copper	$Cu - Cu^{2+}$	$+ 0.337V$
	Mercury	$Hg - Hg^{2+}$	$+ 0.788V$
Noble or cathodic	Silver	$Ag - Ag^+$	$+ 0.799V$
	Palladium	$Pd - Pd^{2+}$	$+ 0.987V$
	Platinum	$Pt - Pt^{2+}$	$+ 1.2V$
	Gold	$Au - Au^{3+}$	$+1.498V$

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