Efficiency of Corrosion Inhibitors on Cathodic Protection System

*[A]Tobinson Briggs, *[Y]obioma M. Eseonu

*Mechanical Engineering Department, Faculty Of Engineering, University Of Port Harcourt, East-West, Choba, Port Harcourt, Nigeria.

ABSTRACT

This study is on experiment being carried out to determine the efficiency of in inhibitors on catholically protected medium carbon steel in sea water in Bonny and Ogbokoro in the Niger Delta region of Nigeria. The experiment was conducted using the total immersion technique in a non-flowing media containing sea water inhibited with potassium dichromate, sodium nitrate, ECIO21A, sarvor CK 368, and Kurizets 636. In the course of this research work, Cathodically protected and unprotected medium carbon steel were totally immersed in seawater containing the aforementioned inhibitors differently. Their weight loss, corrosion rate, pH value and corrosion potentials were determined at intervals of 72 hours, over 2016 hours the test lasted. The results obtained shows that inhibitor EC1021A has efficiency of 79.8%, other results are as follows: Kurizet S.636, 77%, savor CK368, 43%, potassium dichromate, 35% and sodium nitrate, 1.88%. It was concluded that EC1021A is the most efficient inhibitor, under a non-flow system.

KEY WORDS: corrosion inhibitors, Cathodic protection, sea water, non-flow system

1. INTRODUCTION

Due to the toxic nature and high cost of chemicals currently in use, it is necessary to develop environmentally acceptable inhibitors that will be able to beat corrosion on cathodically protected pipe lines. The selection of a corrosion inhibitor is primarily dictated by the system to be treated and the application method. In this study, the primary focus will be to determine the right inhibitors to be used on cathodically protected steel in sea water. The objectives of this study are to evaluate the performances of the various inhibitors and the ultimate proof of its effectiveness on cathodically protected pipe line in sea water. To investigates other parameters such as, pH, weight loss and the corrosion potential of the metal. Make recommendations on the most effective inhibitors. This study will attempt to make a design of cathodic protection system which will provide the desired medium to carry out the cathodic protection test. This will cover the   study on the corrosion environment at which the pipeline corrodes. Also this work will test the weight loss of various coupons to be used i.e. the (medium carbon steel). Thus, this will facilitate the degree of resistance to corrosion when cathodically protected. Finally, perform an efficiency test on various types of inhibitors. This study involves an experimental analysis of cathodic protection test and the investigation of the effectiveness of inhibitors on the various cathodically protected carbon steel. There will be design and installation of cathodic protection system and the method used is complete immersion method.

2.1   EXPERIMENTAL MATERIALS

The sample used for this study consists of coupons made of medium carbon steel. The chemical analysis of the coupon as carried out on a spectrometer is given in Table 2.1. The coupons used for the corrosion study were cylindrical in shapes measuring 43mm diameter and 4mm length and surface area of $0.34m^2$. The medium carbon steel was obtained locally. Other materials used are the corroding medium --seawater, inhibitors from oil industries and laboratories. The inhibitors are, potassium dichromate, sodium nitrate, EC1021A, kurizet S636, and sarvor CK368, electric (digital) weighing balance, plastic brush, beakers, copper wire, flexible string, degreasing agent(acetone), 2volt rechargeable batteries, graphite electrode, others are high resistance voltmeter for Cathodic Protection measurement, pH meter, copper-copper sulphate reference electrode.

2.2   CORROSION ENVIRONMENT

The corrosion media is seawater, various sample of seawater were collected and at different location and period. Their various pH levels are:

Ogbogoro River   -   6.37 at 28^oC

Bonny River   -   7.53 at 28^oC

After the analysis, the one that has more acidic content was chosen.

2.3   DESIGN OF THE IMPRESSED CURRENT CATHODIC PROTECTION

The total surface area of the sample is

SA = 2πr(r+t)   (1)

Where: SA   =   surface area of the material

r = Radius of the material,   t = length of the material

S.A : 2π x 21.5(21.5+4) = 135.08 x 25.5, S.A   = $3444.5mm^2$ = $0.3445m^2$

Total current requires I

I = SA x Cd x S_F (2)

C.d = design current density, S_F = factor of safety   1.3

I = 0.3445 x $1.0x10^{-3}$ x 1.3,   I = 0.0492A

Anode resistance in water

$$RA = \frac{\ell}{2\lambda}\left(In\frac{4L}{r} -1\right)$$

ℓ = seawater resistivity =15Ωcm,   L= anode length =   5.8cm

r   = mean effective radius = 0.4cm

$$RA = \frac{30}{2\lambda \, x 5.8} \left[\text{In} \frac{4\,x\,5.8}{0.4} -1 \right] = 0.8233 \left[\text{In } 58 - 1 \right] = 0.8233 \quad x \, 3.0604$$

$$R_A = 2.51\Omega$$

2.3.1 Cable resistance

Copper wire length = 1m

Copper wire resistance –= Rc/m = 3080 x 10^{-3}/Ωm

Total cable resistance Rc = 3080 x 10^{-3} x 1.0 = 3.08Ω

Total circuit resistance Rt, Rt = R_A + R_C,   Rt = 2.51 + 3.08 = 5.59 Ω

Output voltage required (V), V = I x Rt = 0.0492 x 5.59,   V = 1.59v

2.4 SPECIMENS PREPERATION:

The medium carbon steel (AISI 1040) obtained locally was cut into sizes by power saw machine in the Engineering and Science Workshop, UNIPORT. The specimens were machined to desired measurements, and drilled. The microscopic property of the specimen was examined to determine the internal structures of the metal.

TABLE 1: The pH values of the various inhibitors

INHIBITORS	pH
Potassium Dichromate	6.24
Sodium Nitrate	7.14
EC1021A	7.41
savor CK368	6.43
kurizet S 636	4.24

TABLE 2: The chemical composition of medium carbon steel

SAMPLE	CARBON	MN	P	S	Si
Medium carbon steel (AISI 1040)	0.24	0.17	0.04	0.04	0.14

2.5 Experimental procedure:

The experimental procedure adopted is the total immersion test method because it has good reproducibility of results. According to Okpala (1997), two set of experiments were prepared, that of weight loss and ICCP system. The first set being weight loss as shown in Fig.1, consists of five set of 250ml beakers, set up with five different inhibitors in each beaker (1, 2, 3, 4, 5). The five beakers were filled with seawater up to 200ml each. The initial weight of each coupon was taken and noted. The coupons were then totally immersed in the beakers which contained 5 percent solution of the various inhibitors.

The weighed coupons were suspended in the 250ml beakers with the aid of string. After every 72hrs of immersion, each of the coupons were retrieved from the beakers and washed with water and then brushed with a plastic brush and dried in acetone. This is to avoid water deposit. This procedure was repeated at various intervals over the period of 2016 hours the experiment lasted.

The respective weight and weight lost of each coupon within immersion period were then determined and the corresponding corrosion rate in millimeter per year (MPY) calculated.

According to the corrosion rate formula (Robert Baboran, 2005),

C.R =   KW/ATD   (3)

        Where:

        K = constant, W = weight loss (g), A = Area of specimen, m^2

        T = Time of exposure, (hours), D = Density of specimen

The next set of experiment was ICCP with the same coupon, inhibitors, seawater and the same quantity. The design of the system and installation was done. The washed and degreased specimens of medium carbon steel were immersed in the various medium of electrolyte and the circuit connected. A battery of 2 volt was used to supply the required current. The steel specimens were placed further away from the anode by 5mm; the potential is measured with high resistance voltammeter at intervals of 72hous. The specimens were washed, degreased and the weight loss `measured. The pH values of the various electrolytes were also taken. The $Cu/CuSO_4$ electrode was dipped into each medium, with the positive end of the voltmeter connected to the top of the $CU/CUSO_4$, and the negative terminal to the specimen. The potential of each medium was taken.
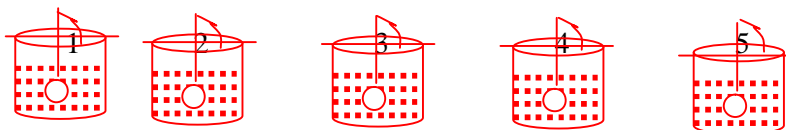

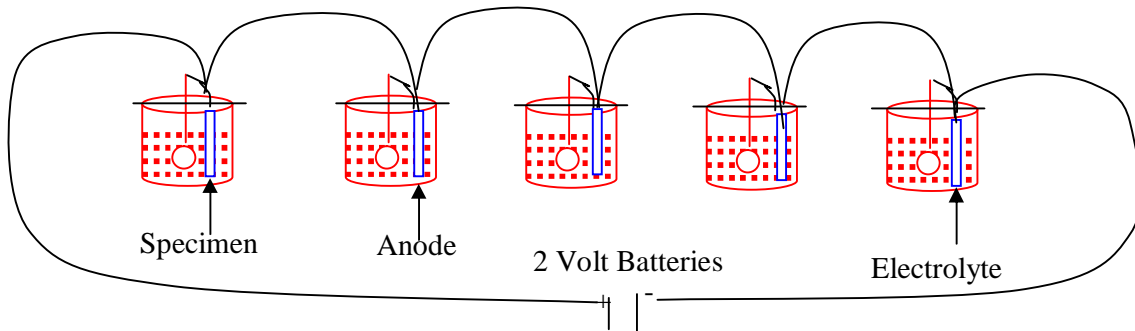**Figure 1 Complete immersion of coupons (Unprotected)**
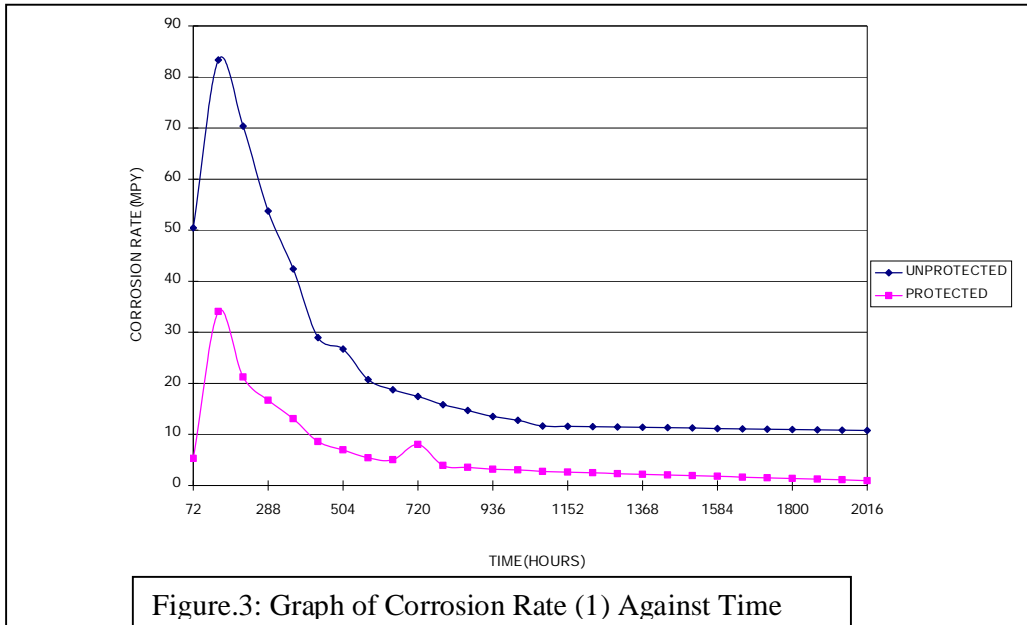
Figure 2 Complete immersions of coupons (ICCP)

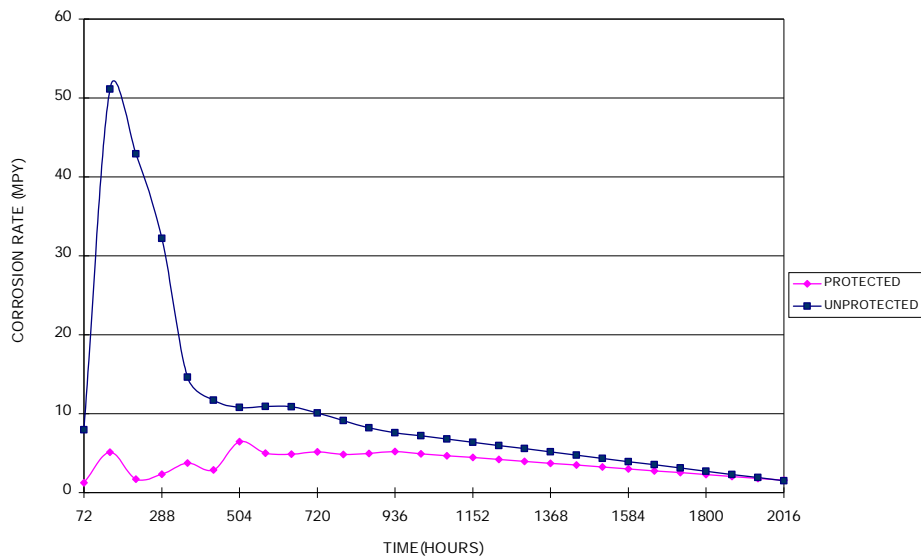Figure.3: Graph of Corrosion Rate (1) Against Time

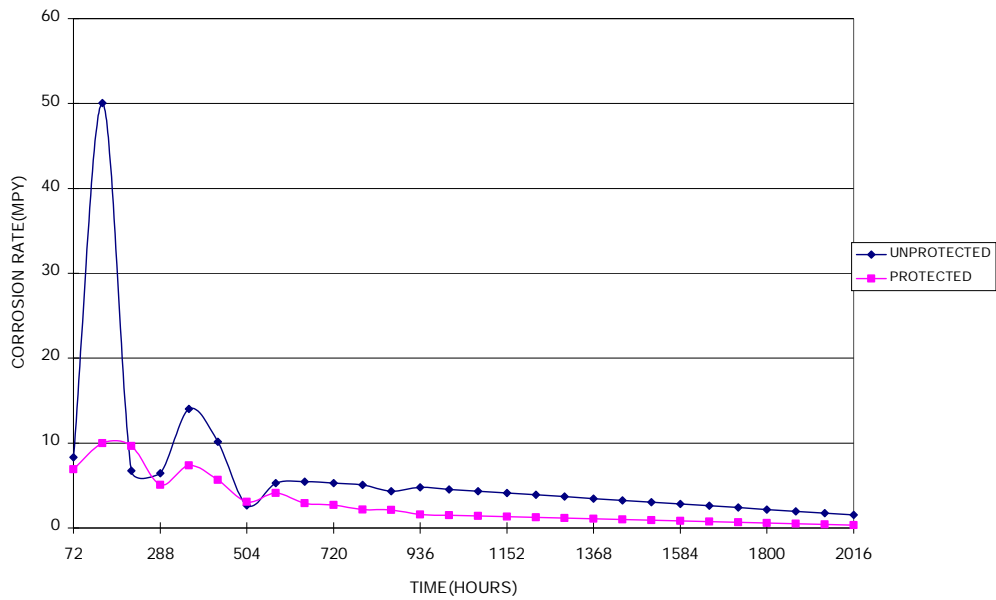Figure.4: Graph of Corrosion Rate (2) Against Time

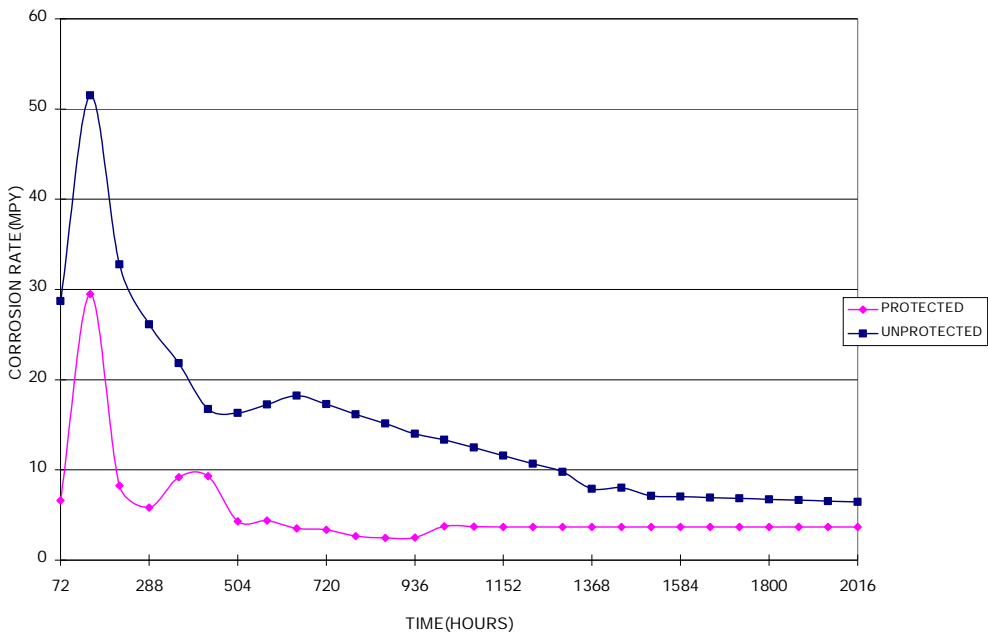Figure.5: Graph of Corrosion Rate (3) Against Time

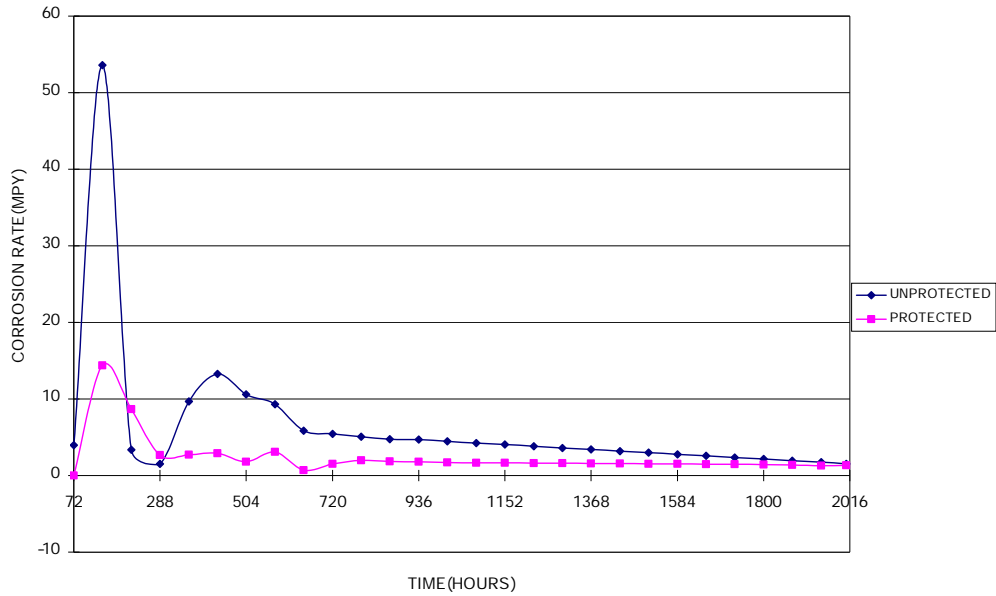Figure.6: Graph of Corrosion Rate (4) Against Time

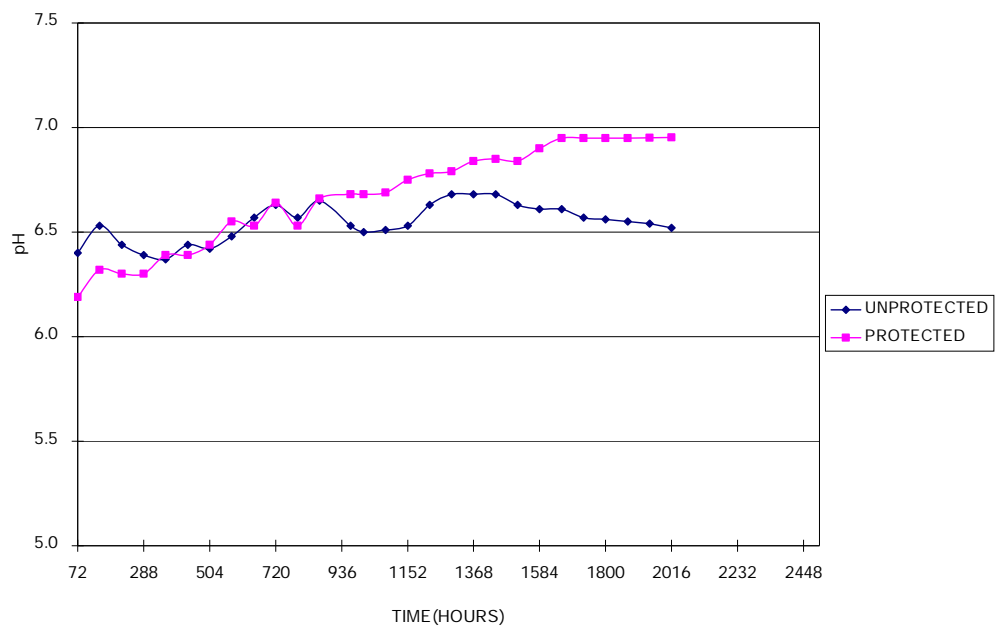Figure.7: Graph of Corrosion Rate (5) Against Time
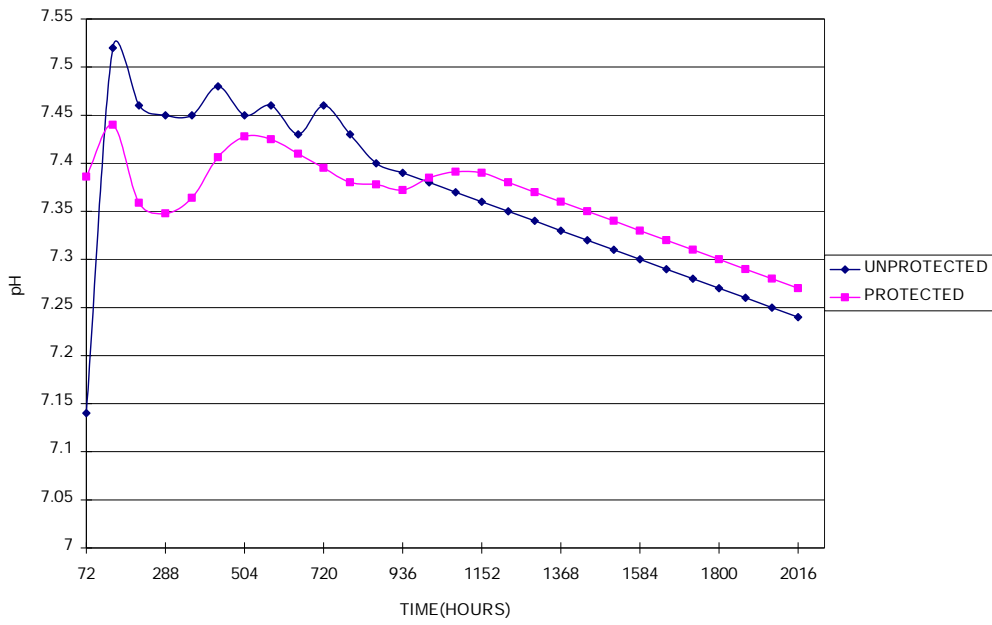

Figure.8: Graph of pH (1) Against Time

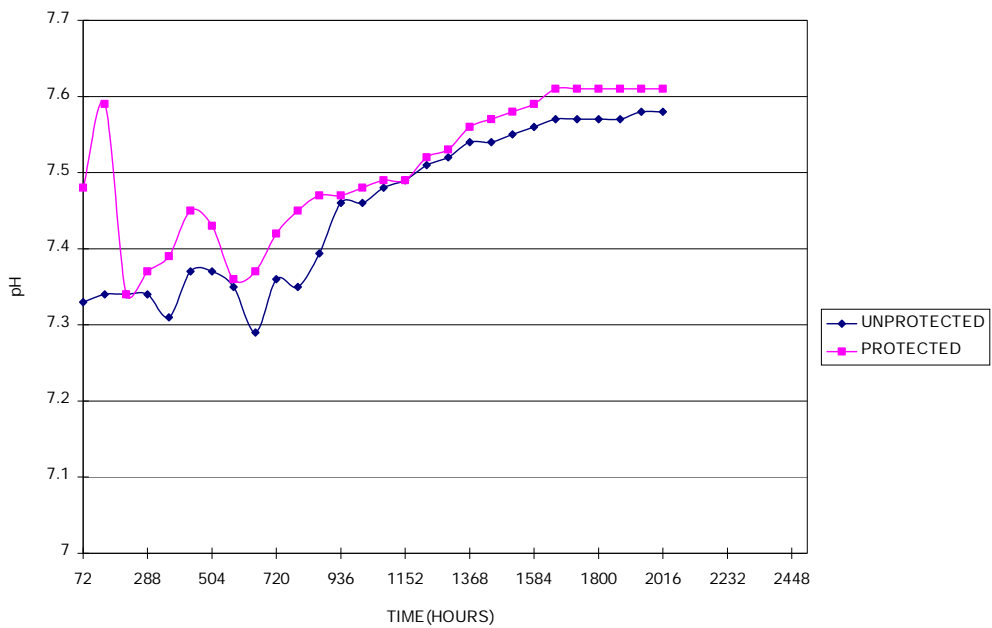Figure.9: Graph of pH (2) Against Time
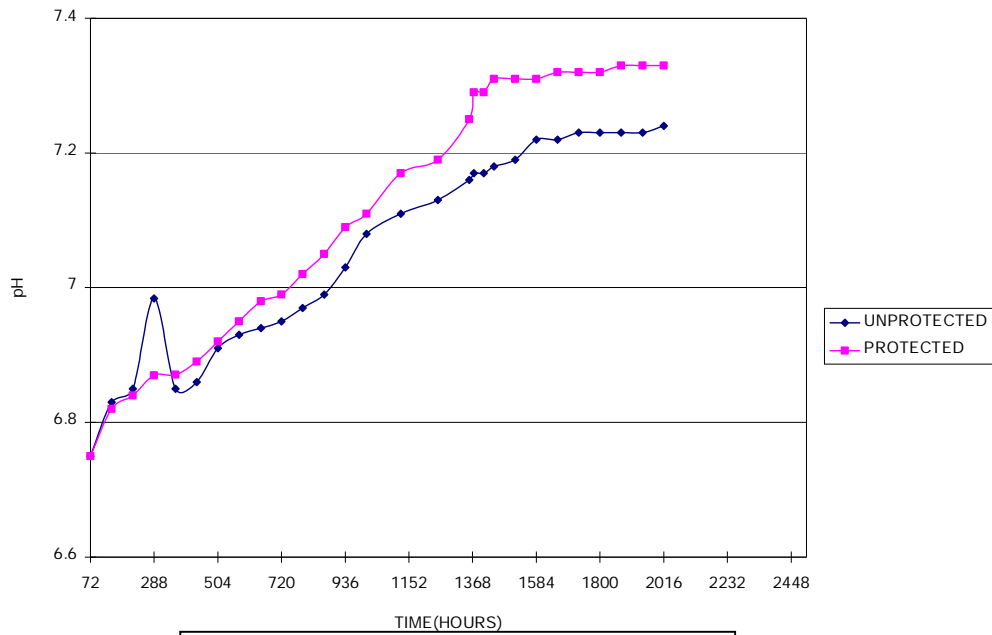

Figure.10: Graph of pH (3) Against Time

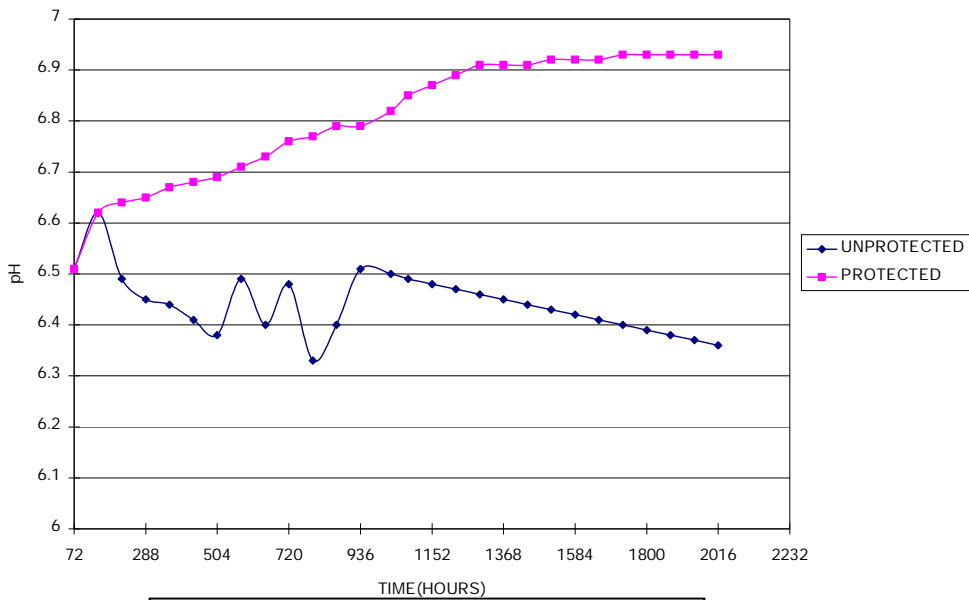Figure.11: Graph of pH (4) Against Time

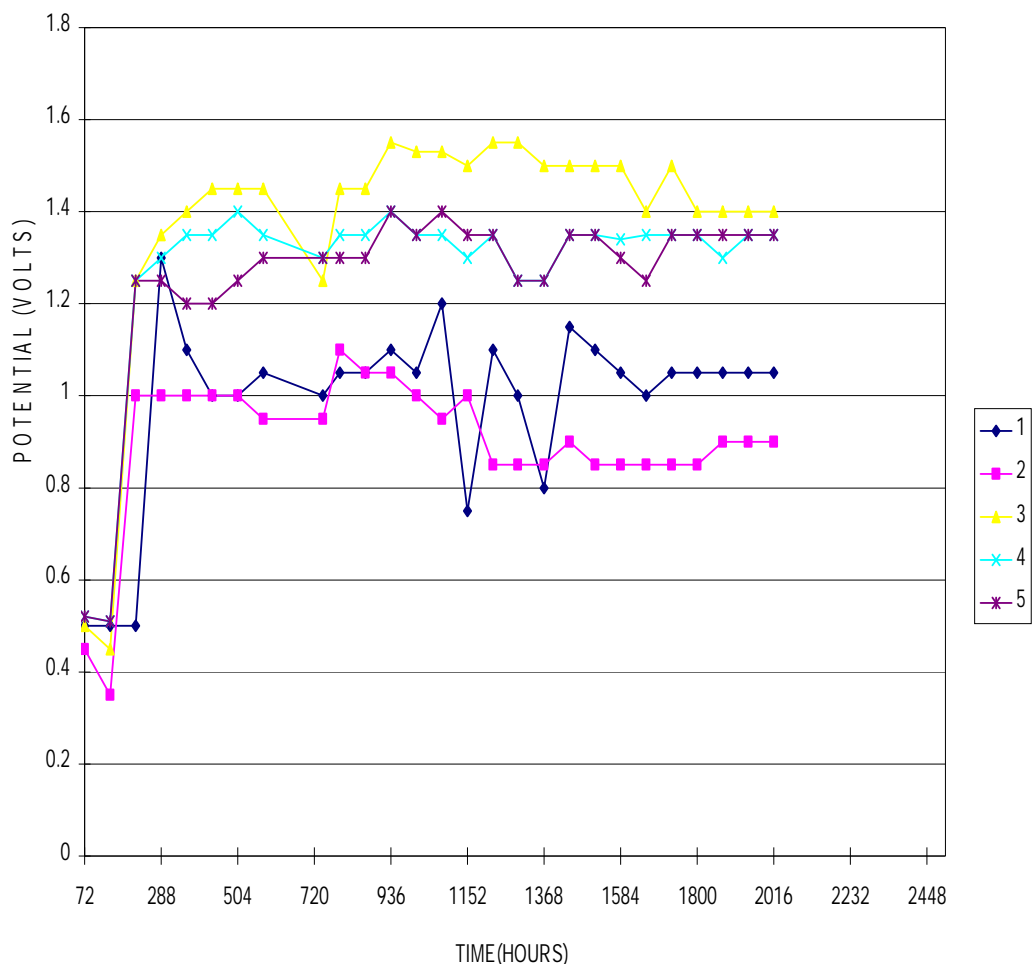Figure.12: Graph of pH (5) Against Time

Figure.13: Graph of Potential against Time

3.1. ANALYSIS AND DISCUSSION OF RESULTS

At the end of the experiments after 2016 hrs, that is 90days, the corrosion rate (C_1R) was calculated for the different samples that is, the 10 tests samples, using the formula:

$$C_1 = \frac{KW}{DAT} \text{ –––––––––––––––––––––––––––––––––––––(4)}$$

The weight loss was determined by finding the difference between the original weight of the coupon and the new weight. The result was recorded between the intervals of 72hours of immersion. The pH value of each of the medium was recorded also at the same interval of immersion as stated above. The result of all the tests and measurements taken are presented and the plots of the results are as shown in figures 3 - 13. After 792 hours of immersing the coupons in the various beakers containing different inhibitors and the corroding medium, bubbles of gasses (hydrogen gas) were observed to evolutes from the beakers at vary degrees. The evolution

of the gas bubbles in samples 1, 2 and 4 inhibited with potassium dichromate, sodium nitrate and Sarvor CK 368 were more than that of 3 and 5 inhibited with EC1021A and Kurizat S 636.

The evolution of gasses on samples 3 and 5 were not too visible. There were brownish suspension noticed especially in media 1, 2 and 4 and is more pronounced in medium 4 which has more oxide formed at the bottom of the beaker. These oxide films were also found in all the beakers but more in samples 1,2,4,5 and 3 accordingly. This indicates that there were heavy corrosion effects taking place in sample 1, 2 and 4 than in samples 3 and 5. It was also observed that there were more passive oxide film at the surface of the coupons of sample 3 and 5. These passive oxide films started gradually forming from 504 hours, signifying protection of the coupons by the various inhibitors at vary degree. Stabilization started from 936hrs for the entire medium.

3.2 For ICCP

The corrosion rates in the various samples were noticed to be more reduced compared to those of unprotected samples. It was observed that hydrogen gas (bubbles) that evolved were reduced, though in samples 1 ,2 and 4 they were more, than in samples 3 and 5. The types of inhibitors used had varying effect on the corrosion rate of the coupon as immersion days increases. After 792 hours of immersion, the corrosion rate decreased in the entire media.

This decrease in corrosion rate must be as a result of the complete exhaustion of oxygen from the electrolyte. The various inhibitors formed a passive oxide film on the surface of the coupons as the time increased, thus preventing further corrosion from taking place.

The impressed current with a buttery of 2volts supplied the required current needed to protect the system. The various inhibitors determined the amount of current flows.

4.1   RESULTS DISCUSSIONS

From the experiments carried out as shown in graph on Figure 1, the corrosion rate for both protected and unprotected specimen rises initially and started to decrease with time as the excess oxygen was observed to have passivated the surface of the coupons. Medium 1, protected and unprotected showed some rise in corrosion rate initially, stabilization started at 792 hours after immersion. The initial increase and decrease of corrosion rate could be due to the non stabilization of the passviating oxide. It showed that the corrosion rate for cathodically protected steel is reduced compared to that of unprotected sample. Figure.2 shows also the corrosion rate of protected and unprotected steel in seawater, i.e. medium 2, as immersion time increased the rate of corrosion decreased. There is sporadic increase in corrosion rate for unprotected at 288

hours compared to protected medium. After 288 hours stabilization started, the unprotected sample showed a higher corrosion rate to protected steel.

In figure 3; Medium 3 showed a different trend, i.e. protected and unprotected. There is a little sporadic increase for unprotected steel up to 51mpy, later there was a drastic decrease. Stabilization started from 576 hours and remains stable till the end of the experiment. There was little difference between CR of protected and unprotected from the plots. Figure 4: Medium 4: shows initial increase in corrosion rate in both protected and unprotected samples. The decrease for unprotected is observed to be gradual from the curve, stability started at 648 hours for protected, while 1368 hours for unprotected. The protected has less corrosion rate compared to unprotected. The stability of the protected steel for medium 4 is more than the other media.

Figure 5, shows a sporadic increase of corrosion rate for unprotected and a drastic decrease. There is fluctuation in increase and decrease of the corrosion rate between 72hours to 504 hours after immersion, stabilization started at 720 hours. The cathodically protected steel has a minimum corrosion rate than the unprotected steel.

4.2   INHIBITORS EFFICIENCY

Inhibitors can affect both parts of the corrosion reaction; the anodic metal dissolution as well as the cathodic reduction of an oxidizing agent. There is a danger of local corrosion if inhibition is incomplete owing to too low a concentration of inhibitor. This danger does not exist with cathodic inhibition. The protective action Z of an inhibitor in percent is defined as;

$$Z = \frac{W_O - W_i}{W_O} \; X \; 100 \; ------------------------------(5)$$

Where;

W_o = metal removal rate with inhibitor (unprotected) in mpy

W_i =   metal removal rate with inhibitor (protected) in mpy

4.3   CORROSION RATE

Inhibitors efficiency

1	2	3	4	5
10.75	1.59	1.54	6.44	1.53
6.95	1.56	0.31	3.66	0.35

$$\text{Medium1} = \frac{10.75 - 6.95}{10.75} \; x \; 100 \; = \; 35\% \quad , \quad \text{Medium 2} = \frac{1.59 - 1.56}{1.59} \; x \; 100 \; = \; 1.88\%$$

Medium 3 = $\dfrac{1.54 - 0.31}{1.54}$ $x100$ = 79.8% ,   Medium 4 = $\dfrac{6.44 - 3.66}{6.44}$ $x\ 100$ = 43% ,

Medium 5 = $\dfrac{1.53 - 0.35}{1.53}$ $x\ 100$ = 77%

5.1   CONCLUSION

After the 2016 hours (i.e. 90 days) period of total immersion, it became clear that the various inhibitors displayed their various degree of efficiency in seawater, both in protected and unprotected media. This thesis presents the efficiency of inhibitors on cathodic protection system. So, from the experiment, result obtained and analysis made the following conclusions may be drawn, i.e. that inhibitor – EC1021A i.e. (sample 3) has better inhibitive efficiency than the rest of the inhibitors. It is also clear that the Cathodically protected medium shows greater efficiency and less corrosion rate than the unprotected medium. The corrosion rate was observed to be higher in –potassium Dichromate (1), Sodium Nitrate (2) and Sarvor CK 368(4) than in EC1021A (3) and Kurizet S 636 (5). The pH value of these media show considerable increases with time as the corrosion rates decreased. Initially pH values were low while the corrosion rate was high. There was stability in all the medium toward the end of the 2016 hours the experiment period lasted. This is as a result of the stabilization of the passivating oxide film in the entire medium. Medium 3 shows very high potential than the rest media, follow by 5 in the cathodically protected system. This system shows greater efficiency of the inhibitors and corrosion rate compared to the unprotected system. This shows that the design of the cathodic protection system and the power supply were adequate to reduce corrosion rate.

5.2   RECOMMENDATION

From the analysis and conclusion of the results obtained, it is therefore recommended that in corrosion studies of efficiency of inhibitors in seawater environment on both cathodically protected steel and non-protected steel inhibitor EC1021A- medium 3, should be used. This is for non flow medium. Also, an alternative to inhibitor 3 is inhibitor in medium 5 (Kurizet S636) which is close to inhibitor 3 in efficiency. Inhibitor 3 has an efficiency of 79.8%, inhibitor 5 - 77%, and inhibitor 4 - 43%, inhibitor 1 - 35%, while inhibitor 2- 1.88%. It is recommended that future work should be on varying the percentage of the inhibitors to ascertain the actual concentration required for a given volume of the corroding medium.

REFERENCES

Akhigbemidu, C. O. (2005): "Prediction of Corrosion Induced failures in Oil and Gas Pipeline". M. Eng. Thesis.

Amula, E. and Okpala, A. N. (2005): "Effect of Corrosion Inhibitors on the Corrosion Rate of Low Carbon Steel in Oil and Gas Environment". NICA, Volume 3. (December Edition 2005)

Eugene, A. A. and Theodore, B. III (1997): Marks Standard Handbook for Mechanical Engineers. Tenth Edition, McGraw-Hill.

Ewald, H. and Henkhaus, R. (1992): Corrosion Science. "An Experimental Approach". Institute of Corrosion, Ellis Horwood Limited

http://www.corrosion-doctor.org/cp/introduction.htm

http://www.engineeing-expert.com/cathodic.html

Kenneth, R. T. and Charmberlain, J. (1998): Corrosion for Science and Engineering. Second Edition. Addison Wesley Longman Limited

Mars G. F. (1986): Corrosion Engineering. 3rd Edition.

Marshall, E. P. and Peattie E .G (1999): Pipe Line Corrosion and Cathodic Protection. "A Practical Manual for Corrosion Engineers" Third Edition. Gulf Professional Publishing Mc Graw Hill.

National Association Of Corrosion Engineers (2000), 89, 79. Corrosion Control In Petroleum Production.

Okpala, A. N. and Uhunmwangho R. (2005): "Corrosion Behaviour of Cathodiclly protected steels in brackish water and simulated seawater". NICA, Vol. 3 (December Edition).

Onuchukwu, A. I. (2005): "The trends of chemical–induced Corrosion Failure,". NICA, VOL 2 (January Edition).

Robert, B. (2005): ASTM International Handbook on corrosion Test and Standard. 2nd Edition

The Holy Bible: Genesis Chapter 3 Verse 9. King James Version.

Umezurike, C. (2001): Engineering Material Design: Properties Selection and Uses, 1st Edition, PAM Unique Publishers, Port Harcourt.