

Cathodic Protection as a Corrosion Prevention Method in Chemical and Marine Industries

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ABSTRACT

The study was carried out to show how cathodic protection can be used to protect steel plate as an alternative to corrosion prevention method in a chemical or petrochemical industries and marine environment. Cathodic protection was carried out in the laboratory by dipping two metal plates one protected and the other unprotected in a solution of 4% NaCl. At intervals of time (days), the unprotected steel corroded with deposit of brownish iron III chloride and the protected steel did not corrode. The weights of the protected and unprotected steels before the experiment (corrosion) were both 179 g, and after the experiment were 176 g and 162 g respectively. The study showed that corrosion rate is inversely proportional to concentration of the electrolyte and time; and, the graph of voltage versus time revealed that the voltage of unprotected steel decreases sharply while that of protected steel decreases slightly.

Key Words: Corrosion, Cathodic, Sodium chloride, Concentration, Time.

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1.0 INTRODUCTION

Adequate protection of materials from corrosion- a gradual destruction, degradation, disbanding of coating from holiday and deterioration of materials due to the reaction between the materials and their environment is inevitable. The reaction can be chemical, electrochemical or metallurgical in nature [1]. Corrosion in metals, whether in the atmosphere, underwater or underground, is caused by a flow of electricity from one metal to another; or from one part of the surface of a piece of metal to another part of the same metal, when conditions permit the flow of electricity [2,3].

Climatic conditions such as humidity, rains or ground water, some environmental and pollution activities influence corrosion of materials [4]. Socioeconomic situations like inadequate trained personnel and un-availability of requisite materials and tools also affects corrosion [2,5].

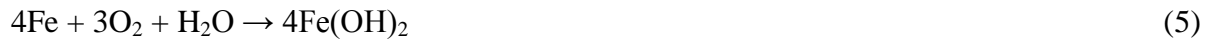
Corrosion of a piece of metal M (e.g. steel pipe) may be summarized as the charge from the metal to the metal ion or the loss of one or more electrons from the metallic atom [6]. This can be written for iron as:



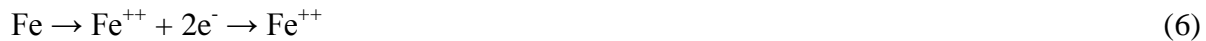
Thus oxidation reaction (the loss of electron) takes place on the anodic site. In order to maintain the electric neutrality of the aqueous environment, the electrons produced by anodic reaction are used in another reaction taking place in the cathodic site.



In solution gas hence, the formation of rust by electrochemical reactions may be expressed as follows:



The most stable form of rust is Fe_2O_3 . At higher temperatures (900-1300 °F), Fe_2O_3 reverts to Fe_2O^+ . From the above equations it is clear that if a piece of iron is placed in water, the metallic iron goes into solution as ferrous ions and the metal assumes a negative charge from the excess electron that remain in it. A sort of equilibrium is reached when the attraction due to this negative charge on the metal is sufficient to prevent any more iron ion from leaving the metal. Due to the difference in charge between the metal and the solution, electrode potential is developed. The transfer of matter is accompanied with the passage of current.



The rate of dissolution of a metal electrode is directly proportional to the amount of current that flowed and also, the amount of metal dissolved is proportional to the total charge passed [7].

Corrosion does not only occur as a result of electrochemical reactions or chemical reactions, but may also be aided by other factors which are either external or internal factors. Some of the factors influencing corrosion include:

1.1 Hydrogen ion concentration (pH) - pH is an important index of the corrosive tendency of a solution or an environment [8]. It influences corrosion in two ways:

- **Directly:** increasing the hydrogen ion concentration causes the potential of the hydrogen electrode to become more positive. A decrease in pH will enhance the cathodic process of hydrogen and oxygen depolarization. This leads to an increase in rate of corrosion, particularly if the corrosion process is chiefly controlled by the hydrogen ion discharge.

- **Indirectly:** A change in pH values of a solution influences the solubility of the corrosion products and the possibility of the protective film formation. Depending on the nature of a metal oxide, corrosion rate increases with either an increase or decrease in the solution pH value [9]. Other factors include temperature, corrosion products (passive film), dissolved CO₂, dissolved salt and many others.

There are many ways by which corrosion may be prevented or minimised. These include the following: design changes, material selection, coating, anodic and cathodic protection.

- ❖ **Design changes or modification** - modification of plants, equipments, and processes can drastically reduce the occurrence of corrosion failure. This is usually made during the exploitation of the equipment process. As the experience is gained in handling these plants and processes, data collected will assist in modification process. Therefore it becomes imperative that logging of all failures should be carried out with the ultimate aim of using them at a later stage in the modification process [10].
- ❖ **Material selection** - material technologist and design engineers consider a large number of factors when selecting for the prevention of corrosion failures. Not only the ability of the material to do the job but also for instance, cost process ability, availability of raw materials and environmental matters.
- ❖ **Coating** - Corrosion resistance can be imparted to metal by coating it with metal. Metallic coatings are either sacrificial or noble with respect to their substrate. Sacrificial coatings, such as aluminium or zinc on steel, will corrode in preference to any underlying metal exposed at pores, scratches, or cut edges; this is due to their higher ionization potential compared with the parent metal. The thicker the coating, the longer this small-scale cathode protection continues. This method is mostly used to protect steel, water and fuel pipelines, storage tanks, steel pier piles, ships, and so on [8,11].
- ❖ **Anodic protection** - oxide layers formed by some metals in the atom are most useful if they are physically tough and damage resistant. In any case, if the damage should occur, the protective layer rapidly reforms. Thicker coatings may be obtained by anodizing that is by anodically polarizing the material by electrolysis with some cathode in a suitable electrolyte. Inhibiting reactions form an important part of corrosion prevention. Any material which inhibits, either partially or completely, the initial reaction at local anodes and cathodes comes within this category. Anodic inhibitors are species which can complex with anodically formed metal ions to produce protective layers. It is however, vital that such species should be present in sufficient concentration to give protection at all local anodes, otherwise corrosion at a relatively few unprotected sites will cause extreme damage [12].
- ❖ **Cathodic protection** - cathodic protection is one of the ways of protection of metals (mild steel) against corrosion and thus, can be defined as corrosion prevention method where by a metal to be protected is used as the cathode. It is also an electrochemical means of corrosion control in which the oxidation in a galvanic cell is concentrated at the anode and suppresses corrosion of cathode in the same cell. If the protective layer is of a less

noble metal, such as in the arrangement in galvanised objects and other situations where zinc prevents iron from corroding, zinc becomes the anode and iron the cathode so that the status of the iron is preserved. This encouragement of an alternative corrosion process to the one causing harm is known as ‘cathodic protection’ and is employed extensively in the protection of metals in marine use and in pipelines [12,13].

Cathodic protection is unique among other corrosion prevention methods considering its economic design, construction, operation, and management of systems and subsystems in which matters undergo conversion. Cathodic protection of systems minimizes cost and increases their long time of usage. Cathodic protection has found its way into petroleum industry in which most of the devices and facilities used in crude oil production such as pipe lines, storage tanks, separators, stabilizers, scrubbers, pumps, and compressors. They are in continuous contact with fluids and for time of usage, they have to be cathodically protected. If the corrosion is unchecked the result will be perforations in pipe lines, tanks vessels, reduction in thickness and eventual collapse [14].

Cathodic protection has helped both government and individuals to use little proportion of their annual budget to combat corrosion in order to reduce engineering failures due to it. Platform or metal in sub-sea zone are usually cathodically protected from corroding in this zone. Cathodic protection can also be used to protect pipes [5,9].

There are two ways to cathodically protect a structure namely: by an external power supply (impressed current) and by sacrificial anode [9,13]. The two ways can be compared as contained in Table 1 [15]:

Table 1 Comparison of sacrificial anode with impressed current

Sacrificial anode	Impressed current
Simple	Complex
Low and no maintenance	Required maintenance
Work best in conductive electrolytes	Can work in low conductive electrolyte
Lower installation cost for smaller installations	Remote anode possible
Higher capital investment for large systems	Low capital investment for large system
Require material anode to the protected steel	Anodic material may not necessarily be anodic to steel
Voltage difference between anode and cathode are limited approximately to 1 volt or less	Voltage difference between anode and cathode are large

However, since engineering is much concerned about minimum cost in designing, sacrificial anode systems are generally preferred for pipes, gaskets, pumps, because of their simplicity and stability [9].

The increase in reports and records of pipes, tank vessels and other engineering infrastructures in both households and industries prompted this study and demonstration of cathodic protection of a mild steel plate and its choice over other corrosion prevention methods.

This research is aimed at investigating use of cathodic protection as an alternative corrosion protection. This involves exposing two steel plates, protected and unprotected to similar corrosion liable conditions to test their proneness to corrosion.

2.0 MATERIALS AND METHODS

Sodium chloride pellets of analytical grade was purchased from a chemical shop in Port-Harcourt Nigeria and used without further purification. Voltmeter, retort stand, silver-silver reference electrode, electronic weighing balance, plastic bucket, measuring cylinder, beakers, drilling machine, and meter-rule were also used for the study.

About 1100 cm³ volume of distilled water was measured into a plastic bucket where 44g of NaCl pellet was added to make 0.04g/dm³ of NaCl solution. The solution (4% NaCl) was then thoroughly mixed and kept for further use. Two mild steel plates (30 by 10 cm) were cut; one of the plates was protected by the attaching zinc anode through hole drilled at its centre while the other plate was left unprotected. The plates were then dipped into the sodium solution. Silver-silver chloride reference electrode was then connected to a voltmeter and the tip (terminal) of the electrode was made to have contact with the solution and plate. Voltage drop across the plates were then read on the voltmeter, denoting the degree of corrosion of the plates. The masses of the plates before and after the experiments were measured.

2.1 Statistical analysis

Regression line (least-square) or line of best fit is a concept based on the gradient intercept form of equation of a straight line. The mathematical expression for a straight line is given as:

$$y = ax + b \quad (7)$$

where 'a' and 'b' are coefficients representing the slope and intercept, respectively which are calculated as follows:

$$a = \frac{n \sum xy - (\sum x)(\sum y)}{n \sum x^2 - (\sum x)^2}, \quad b = y - ax$$

The correlation coefficient 'r' was used to statistically measure the amount of linear relationship between x and y, this can be expressed as:

$$r = \sqrt{aa'} \quad (8)$$

where a and a' are the slopes of regression line y on x and x on y, respectively. Therefore

$$r = \frac{n \sum xy - \sum x \sum y}{\sqrt{n \sum x^2 - (\sum x)^2} \sqrt{n \sum y^2 - (\sum y)^2}} \quad (9)$$

The above correlation is sometimes called Pearson's coefficient of correlation or Pearson product moment correlation coefficient [16].

3.0 RESULT AND DISCUSSIONS

The general criterion for successful cathodic protection is taken as a potential realised on all parts of the submerged steel of at least 0.8v measured against a silver-silver chloride reference electrode containing the water. The following results were obtained for protected and unprotected steel.

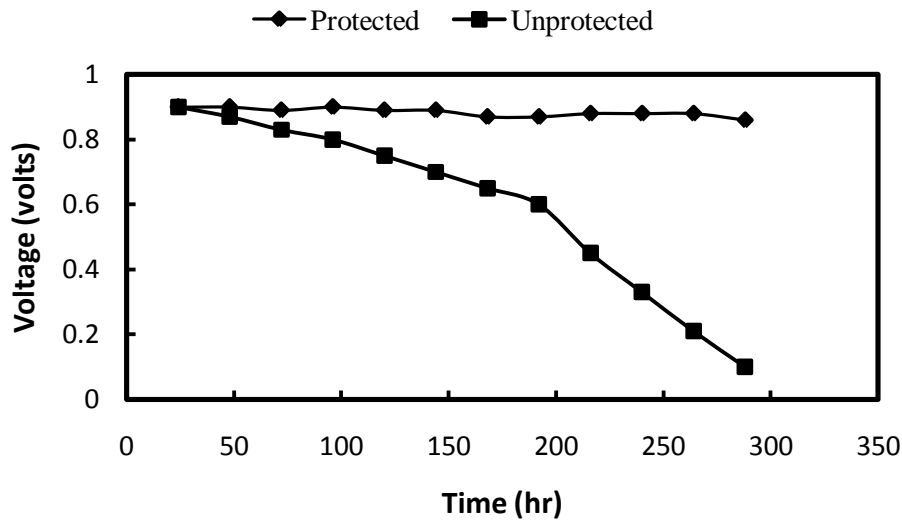


Fig. 1 Corrosion rate (voltage) versus time for protected and unprotected steel

Table 2 Physical properties of protected and unprotected steel

Properties	Protected steel	Unprotected steel
Colour before experiment	Ash	Ash
Colour after experiment	Ash	Brownish due to deposit of $Fe_2O_3 \cdot xH_2O$
Mass before experiment	179g	179g
Mass after experiment	176g	162g

The linear regression equations for protected and unprotected steel are:

Protected steel, $y = 1.0229 - 8.97 \times 10^{-4}x$ (10)

Unprotected steel, $y = 1.067 - 3 \times 10^{-3}x$ (11)

The correlation coefficients for protected and unprotected steels are:

Protected steel, $r = -0.491$ (12)

Protected steel, $r = -0.84$ (13)

3.1 Unprotected steel

As oxidation took place, electrons migrated from the metal to the electrolyte there by reducing the rate of flow of current and consequently, reducing the voltage across the metal. Therefore the rate of corrosion increases because of further oxidation of iron. The behavioural pattern of the iron oxidation with time is shown in Fig. 1

Colour change from ash to brown after the experiment was observed on the unprotected metal steel as reported in Table 2. This is as a result of deposition of brown hydrated iron III oxide $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ which is similar to the equation of reaction (5). Colour change was used to monitor corrosion behaviour in a study carried out on application of the multichannel electrode method to monitoring of corrosion of steel in an artificial crevice [17]. To further confirm that the unprotected steel was depreciating in its matter content in the course of the rusting (experiment), the masses were found to be 179 g and 162 g before and after the experiment, respectively.

The regression equation (11) obtained represent the regression line which shows the linear relationship between the voltage drop in cathodic unprotected steel plate as a function of time. Hence, it can be used to predict the voltage at any given time in unprotected steel.

The degree of their correlation r (-0.84), satisfies $-1 \leq r \leq 1$ and is close to -1. The time(x) and voltage (V) are highly negatively correlated. This shows that as time increases the corrosion rate increased.

3.2 Protected steel

The principle of using zinc anode to protect steel from rusting an object made of iron or protecting with another metal that does not corrode so easily was adopted [8]. Zinc was used to protect steel because it is higher than iron in electrochemical series and highly reactive [11].

In cathode protection of steel, zinc which is above in electrochemical series, served as the anode. As the zinc layer was broken, the zinc dissolves instead of the iron; iron being the cathode remains intact. Rusting of iron will only set in after all the zinc has corroded; thus, zinc formed an efficient protective covering for iron. This can be seen from the plots of the protected profile in Fig. 1. The coated iron by zinc did not show any significant changes throughout the period of study with the linear-horizontal nature of the graph. Physical observation of the iron steel also showed its' unchanged colour before and after the experiment.

The use of mass differential of material for assessing corrosion activities is a vital phenomenon in corrosion studies [18,19]. The mass of the protected iron steel before and after the study was steady with slight variation observed; this further confirmed that corrosion was almost passive or negligible. Mass variation was also used to study corrosion behaviors of metals in biodiesel from rapeseed oil and methanol [20].

The regression equation (10) obtained represent the regression line which shows the linear relationship between voltage (corrosion rate) drop in cathodically protected steel plate as a function of time. Hence, it can be used to predict the voltage at any given time in protected steel.

The correlation coefficient r (-0.491) satisfies the inequality $-1 \leq r \leq 1$ and is not close to -1. This is a linear correlation. Therefore, time and voltage are slightly negatively correlated signifying that as time increases, the corrosion rate did not increase.

CONCLUSION

The result of the study showed that corrosion rate was inversely proportional to concentration of the electrolyte and time. It also showed the accuracy of cathodic protection as an option for corrosion prevention is high. The results showed that this technique can be used to protect steel materials from corroding which will save time and income.

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