

Effect of Anode Variation and Size on the Cathodic Protection of Mild Steel in Sea Water and Sulphuric Acid

C.A. Loto

Department of Mechanical Engineering

Covenant University, PMB 1023, OTA,

Ogun State, Nigeria.

E-Mail Address: akinloto@yahoo.com;

akinloto@gmail.com

Abstract

The performance of different sizes of zinc, and aluminium galvanic anodes on the cathodic protection of mild steel in seawater and 0.2M sulphuric acid was evaluated at ambient temperature. The magnitude of corrosion protection by the galvanic anodes was observed by weight loss method, corrosion rate calculation and potential measurement technique. It was observed that the aluminium anodes proved more effective as sacrificial anode for mild steel in seawater environment. In sulphuric acid environment, the zinc anode gave a more protective performance than aluminium anode. Potential measurement results obtained were found to correspond with the results obtained from weight loss method. For both environments, the effects of a varying cross-sectional area and the anode material on the cathodic protection of mild steel were examined.

Key Words: Cathodic protection, corrosion, galvanic, impressed current, anodes, seawater, sulphuric acid, weight loss, corrosion rate, potential measurements, zinc, aluminium.

INTRODUCTION

One of the biggest challenges facing our aging infrastructure today is materials loss and deterioration by the electrochemical reactions that cause corrosion. Many government studies

indicate that in the US alone, costs due to corrosion loss is more than \$276 billion annually⁽¹⁾.

Most of the corrosion loss on the infrastructure can be prevented by science and technology that is available to us today.

Among the various methods available to prevent or control corrosion is the cathodic protection technique, which was first used in 1824 by Sir Humphry Davy and described in a series of papers presented to the Royal Society⁽²⁾ in London. Cathodic protection (CP) is a technique to control corrosion of a metal surface by making that surface the cathode of an electrochemical cell. Cathodic protection systems are most commonly used to protect steel, water/fuel pipelines and storage tanks; steel pier piles, ships, offshore oil platforms and onshore oil well casings among others. A side effect of improperly performed cathodic protection may, however, be production of molecular hydrogen, leading to its absorption in the protected metal and subsequent hydrogen embrittlement⁽³⁾. Hydrogen embrittlement is the process by which various metals, most importantly, high-strength steel, become brittle and crack following exposure to hydrogen.

The two mostly used methods of CP are the galvanic or sacrificial anode method; and the impressed current cathodic protection. Galvanic or sacrificial anodes are made in various shapes using alloys of zinc, magnesium and aluminium. For magnesium, the alloy AZ63 (6Al, 3Zn, 0.2Mn) is mostly preferred over the pure magnesium as it prevents pitting of the anode in service. Because of local cell action and corrosion products that form on its surface, a magnesium anode has an efficiency of only about 50%, which means that only one-half its corrosion current flows to the protected structure, the rest is wasted on little local reactions on the magnesium surface⁽⁴⁾. Zinc anodes are usually 99.99% Zn or, for seawater, an alloy with a few tenths of a percent Al and Cd. The potential of zinc is less than the potential of magnesium, at about -1.1V versus copper-copper sulphate (Cu/CuSO₄) electrode but the efficiency is excellent at about 95%.

The electrochemical potential, current capacity and consumption rate of these alloys are superior for CP than iron. A sacrificial anode, or sacrificial rod, is a metallic anode used in an electrochemical process where it is intended to be dissolved to protect other metallic components. Galvanic anodes are designed and selected to have a more “active” voltage (technically a more negative electrochemical potential) than the metal of the structure (typically

steel). Sacrificial protection is inexpensive because it has the obvious advantage that it does not need any external power source. It also gives a fairly uniform distribution of current, but that current output is low and the only way to increase it is to use more anodes. Little or no maintenance is required except to replace the anode, which should be necessary only after several years of service. But because the system is cheap and simple, there is usually no convenient way to monitor the amount of protection being given ⁽⁴⁾.

Examples of the application of sacrificial anodes include the following: ships, hulls, offshore oil and gas drilling rigs, production platforms/semisubmersibles and support underwater pipelines, underground pipelines, buried structures, harbour piling and jetties', floating docks, dolphins, buoys, lock gates and submerged concrete structures. There are many other uses, including a large range of industrial equipment where the surfaces are in contact with corrosive electrolytes, e.g. heat exchangers, pump impellers and vessel internals ⁽⁵⁾.

The impressed current cathodic protection is used for larger structures that galvanic anodes could not economically, deliver current to provide complete protection. Impressed Current Cathodic Protection (ICCP) systems use anodes connected to a DC power source (a cathodic protection rectifier). Anodes for ICCP systems include silicon, cast iron, graphite, mixed metal oxide, platinum and niobium coated wire.

Cathodic protection (CP) is widely applied for corrosion prevention on steel structures in contact with sea water; one of its most important applications is the protection of platforms and submerged structures. Nowadays, the gas and oil production is being developed in deeper waters (between 500 m and 2,000 m). At such depths, maintenance is difficult to carry out, so that reliability of materials and protection systems are very important, as well as the choice of the optimal protections conditions. The environmental conditions in deep water are severe, characterized by the absence of oxygen (then possibly promoting the growth of sulphate-reducing bacteria), the presence of sulphides and neutral to slightly acid pH. All these factors influence the chemical equilibrium (in particular, carbonate and bicarbonate), modifying the protection conditions and affecting the electrochemical behaviour of the anodic material ⁽⁶⁾. A typical ICCP system for a pipeline would include an AC powered rectifier with a maximum rated DC output of between 10 and 0 volts.

The importance of cathodic protection cannot be overemphasized. It has performed a tremendous role in the sustainability and longevity of engineering materials, metals especially, in service. This investigation focuses on a continuous effort being made to improve the efficiency of this method to battle the debilitating effect of corrosion in the society. In this respect, a wider engineering application and the economic benefit is ensured.

This experimental work, therefore, examines the performance of zinc and aluminium alloys as sacrificial anodes for the cathodic protection of mild steel in both sea water and sulphuric acid media. It aims at investigating the effect of varying anode size and the anode material on the rate of corrosion of the test specimens and the corresponding protection effectiveness of the anodes at the ambient temperature.

Experimental procedure

Preparation of specimens

All the metallic materials used in this work, that is, the mild steel, the zinc and aluminium anode plates were locally obtained in Nigeria. The mild steel specimen had a per cent nominal chemical composition of 0.130C, 0.147Cu, 0.173Si, 0.397Mn, 0.017P, 0.031S, 0.010Co, 0.0005Ca, 0.021 Zn and the rest 99.2Fe. The zinc anode used had 99.4 per cent zinc composition and the aluminium anode had 99.7 per cent aluminium composition. The seawater was obtained from ExxonMobil, Qua Iboe Terminal, Eket, Nigeria. The sulphuric acid was of AnalaR grade. The concentration of the acid used was 0.2M H_2SO_4 . The metallic test samples were cut into dimensions of 200mm \times 350mm \times 3mm. They were initially pickled in dilute hydrochloric acid, HCl. These test specimens were then ground with silicon abrasive paper of 60, 120, 220, 320 grits, polished to 1 μm , cleaned thoroughly with distilled water/ethanol, dried and kept in a dessicator for further weight-loss experimental tests. Some selected specimens were, in turn, mounted in araldite resin after spot welding to the connecting insulated flexible wire. They were to be used for potential measurements of the steel test specimens/galvanic anodes (Zn and Al specimens). Aluminium and zinc were the two metals used for the seawater galvanic anodes. The aluminium and zinc sacrificial anodes were also cut into sizes varying with the experimental setup and measurement.

Weighed test pieces were separately and fully immersed for 24 days in each of the beakers containing the 0.2M H₂SO₄ and the seawater in which the test pieces were separately protected by wire connection to each of the aluminium and zinc anodes. Each of the test specimens and the anodes was taken out every three days, washed with distilled water, rinsed with methanol, dried, and re-weighed. Plots of weight loss vs. exposure time and the corrosion rate vs. exposure time were made, Figs. 1-8. Similar experiment as above was done for the unprotected specimens, that is, those that were not protected with aluminium and zinc anodes.

Potential measurements

The prepared test specimens were tested for potential measurements. They were immersed, in turns, in the test media after being connected to the zinc and/or aluminium anode(s). Potential measurement tests were also performed in the different test media for the unprotected test specimens, i.e. those not connected with the Zn or Al anodes. The potential was recorded at every one day interval using a digital voltmeter and saturated calomel electrode as the reference electrode. Plots of variation of potential (vs. SCE) with the exposure time were made as presented in Figs. 9-10.

pH Measurements

The pH measurements of all the different corrosion media both acidic and aqueous environment were taken over a one day interval and their values recorded.

Results and Discussion

When two metals are electrically connected to each other in electrolyte for example, seawater, electrons will flow from the more active metal to the other, due to the difference in the electrical potential, the so called driving force. When the most active metal (anode) supplies current, it will gradually dissolve into ions in the electrolyte, and at the same time produce

electrons, which the least active (cathode) will receive through the metallic connection with the anode. The result is that, the cathode will be negatively polarized and hence be protected against corrosion ⁽⁷⁾.

Weight- loss and corrosion rate of mild steel in seawater

The results obtained for the variation of weight loss with exposure time and the corresponding corrosion rate vs. exposure time for the steel specimens immersed in seawater for the anode protected test specimens and the unprotected ones, are presented in Figs. 1 to 8.

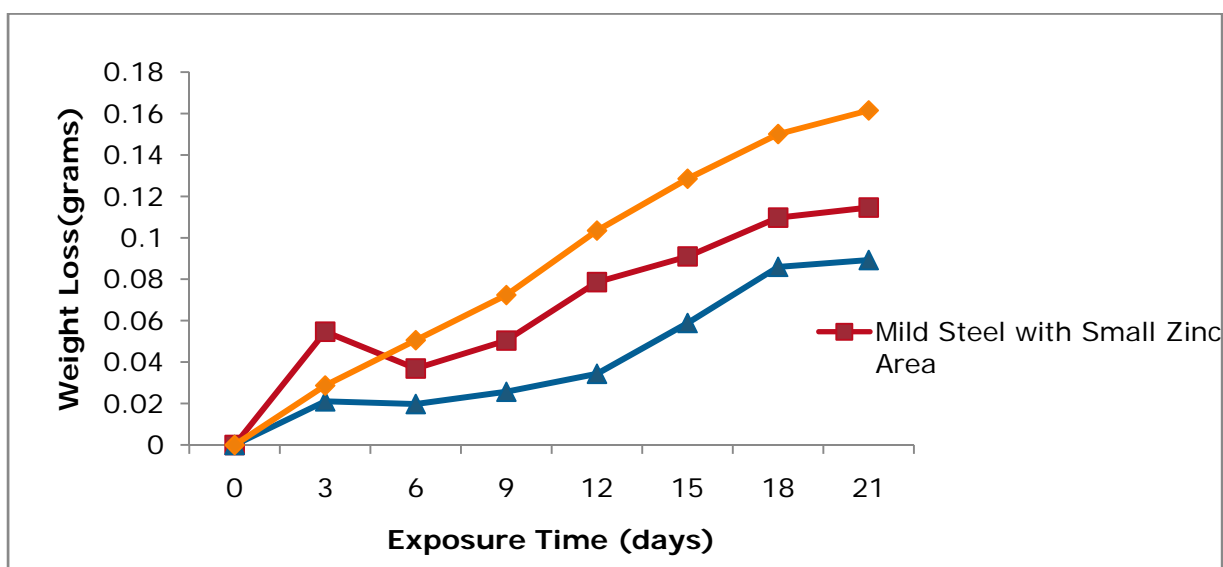


Fig.1. Variation of weight loss with exposure time for mild steel sample immersed in Seawater protected with zinc anodes.

In Fig. 1, it can be observed that there was a minimal rise in weight loss of mild steel in the experiment with the large zinc anode, but a relatively greater weight loss was achieved for the mild steel protected with a small zinc anode. It can therefore be deduced that the rate of loss of metal to corrosion decreases as the area of the zinc sacrificial anode increases. Comparing the results presented in Figs.1 to 3 regarding the protected and the unprotected specimens, the overall positive effect of the sacrificial anode cathodic protection can be clearly observed. In Fig.2, it can be seen that the corrosion rate of mild steel protected with large zinc anode is

relatively more stable and lower than that of the smaller zinc anode. This confirms the impact of the anode size effect on the cathodic protection performance.

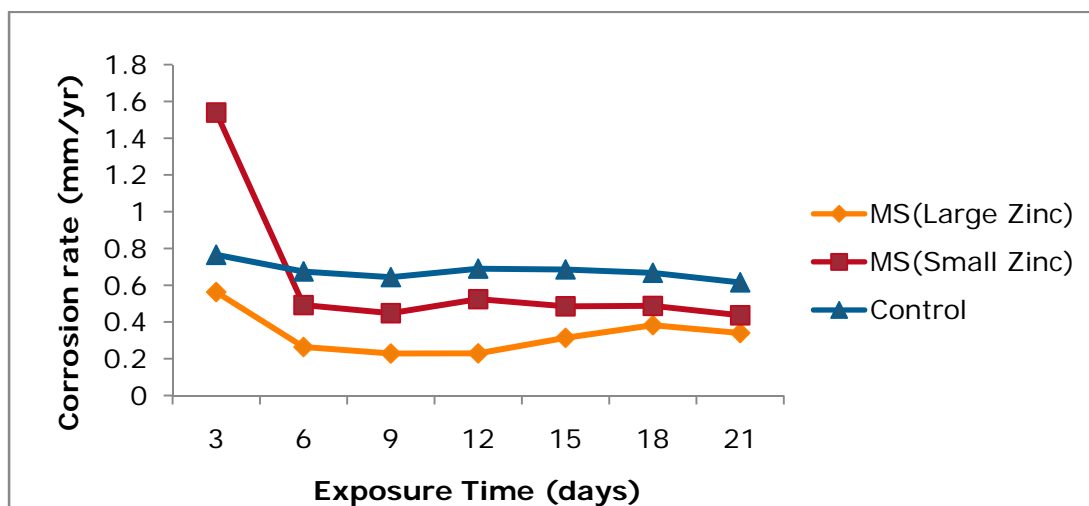


Fig.2. Variation of corrosion rate with exposure time of mild steel samples in seawater with zinc anode.

The results presented in Fig. 3 show and also confirm the more effective cathodic protection performance of aluminium anode for the protection of mild steel in seawater. The aluminium anode proved most efficient as it achieved a maximum weight loss of 40mg over 21 days. The zinc anodes recorded weight losses ranging from 80 to 120mg for the large and small anodes respectively. The better performance of the larger zinc anode than the smaller one is due to size effect. The bigger the anode, the bigger will be the surface area and hence the more the amount of electrons that will be released to protect the cathode.

The corrosion rate of mild steel protected by aluminium anode in seawater as shown in Fig.4, confirms its more protective effectiveness. The corrosion rate decreased with exposure time for most part of the experimental period; and after 9 days of the experiment, it maintained a constant or steady state corrosion rate, thus protecting the mild steel effectively and with very low rate of anode dissolution. Aluminium anode can, therefore, be considered to be more effective and economical than zinc anode in protecting mild steel in seawater.

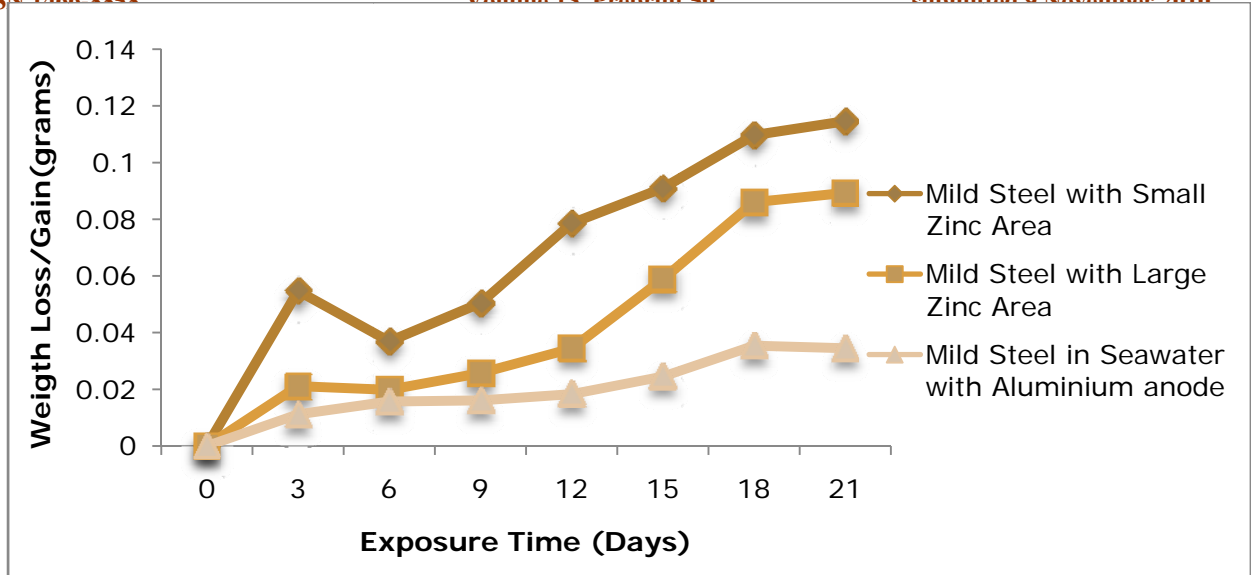


Fig 3. Variation of weight loss with exposure time for mild steel in seawater differently protected with zinc and aluminium anodes.

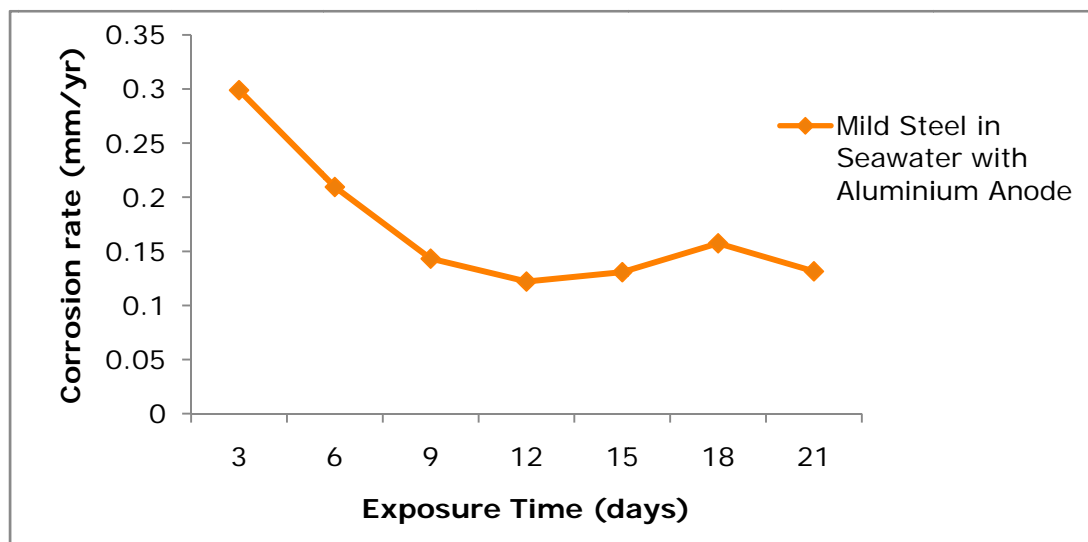


Fig.4. Variation of corrosion rate with exposure time of mild steel protected by aluminium in seawater.

The results obtained for the test specimens immersed in 0.2M H₂SO₄ at ambient temperature and using zinc and aluminium anodes for the cathodic protection of the mild steel test specimens are presented in Figs.5-8. It could be observed, as shown in Fig. 5, that there was a considerable decrease in weight loss of mild steel throughout the experiment when the zinc with a larger cross-sectional area was used as the sacrificial anode. It recorded a maximum weight-loss value of 50mg (0.05grams); the smaller zinc anode achieved a weight loss 90mg (0.09grams) during the same time of the experiment.

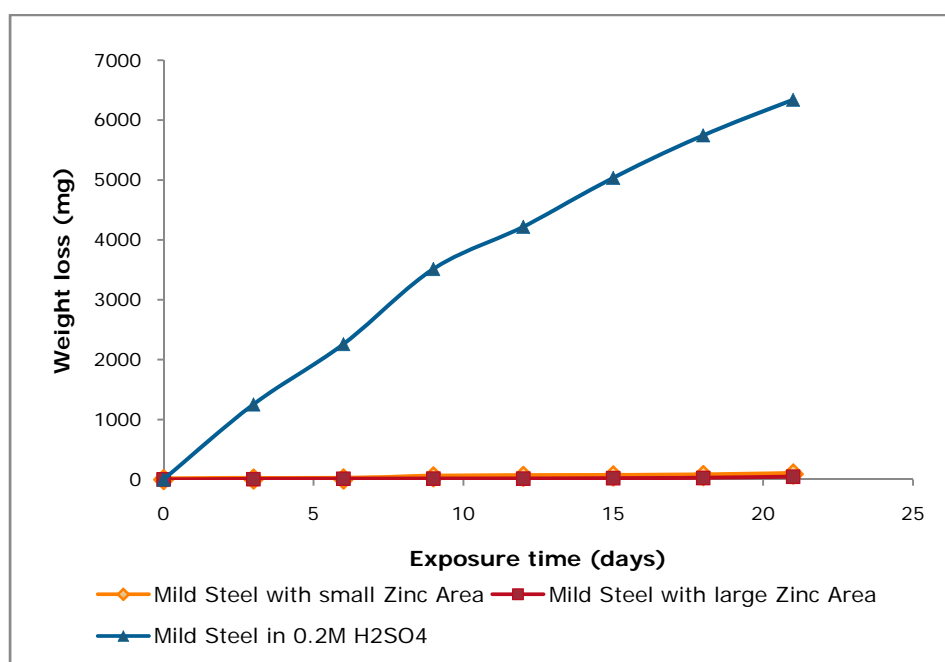


Fig.5. Variation of the weight loss with exposure time of mild steel sample immersed in H₂SO₄ with and without zinc anode.

Unlike the results obtained from the experiment carried out in seawater when zinc was used as anodes, as shown in Fig.1, it can be inferred here that zinc sacrificial anodes are more efficient and will protect the mild steel in H₂SO₄ environment than in seawater. However, with aluminium as the sacrificial anode in sulphuric acid medium at ambient temperature, the weight loss of mild steel increased rapidly to about 350mg (3.5grams) This, indicates that there was quite substantial corrosion occurrence on the mild steel specimen with little protection offered by the aluminium

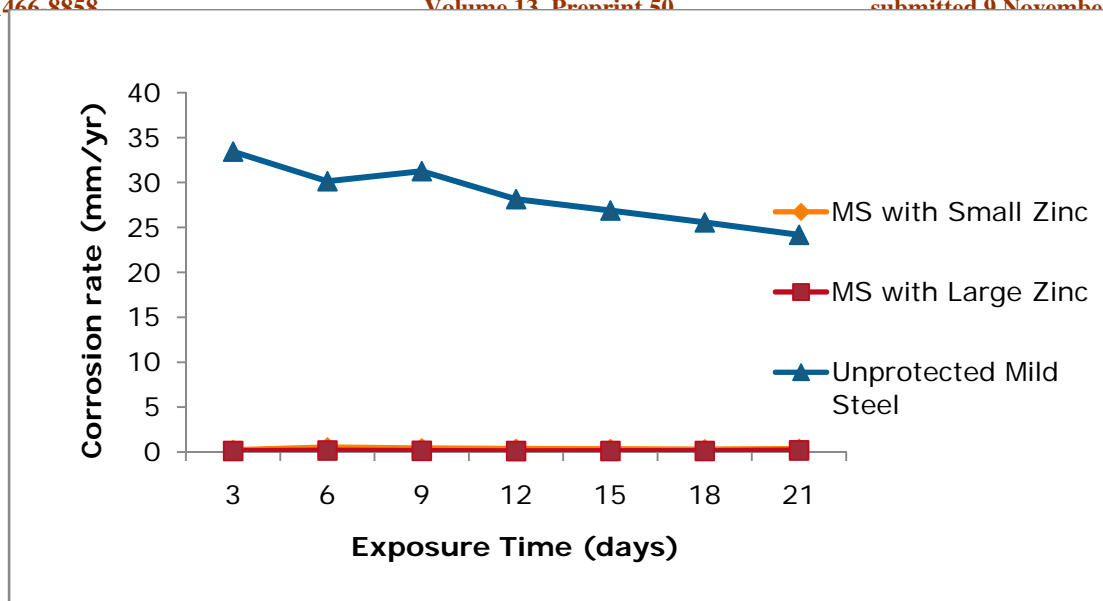


Fig.6. Variation of the rate of corrosion with exposure time of mild steel in H_2SO_4 both with and without zinc anode.

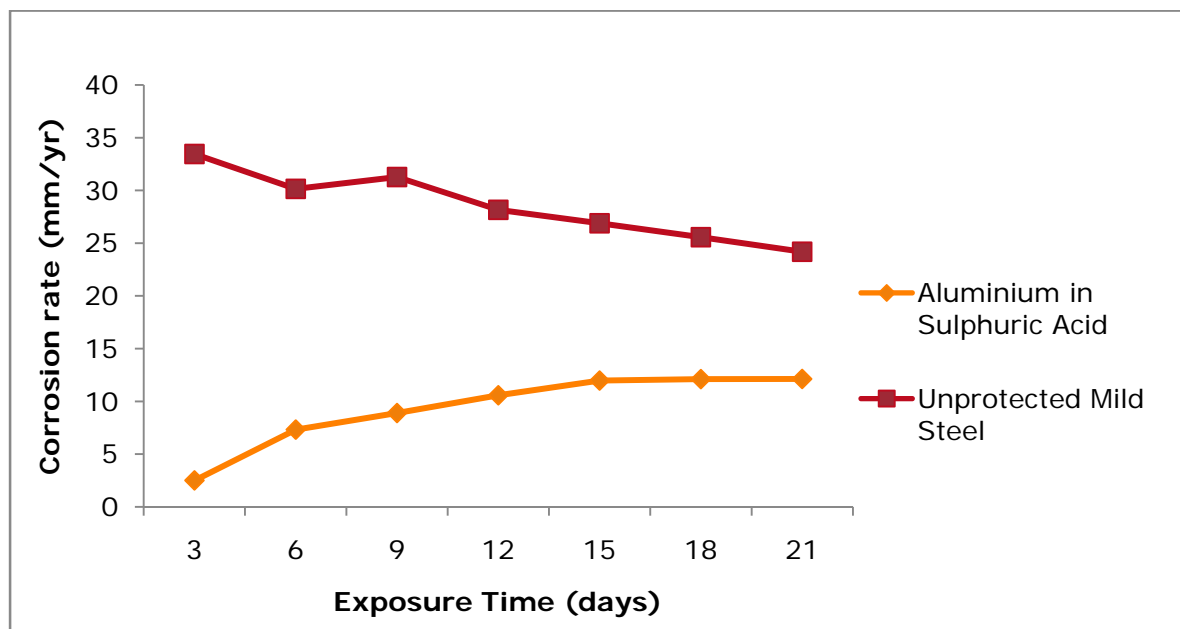


Fig.8. Variation of corrosion rate of mild steel sample with exposure time immersed in sulphuric acid with and without aluminium anode protection.

anode. Consequently, the corrosion rate rose gradually to about 12 mm/yr where it became considerably stable. It could, therefore, be said that aluminium is a relatively poor sacrificial anode for mild steel in H_2SO_4 environment at room temperature.

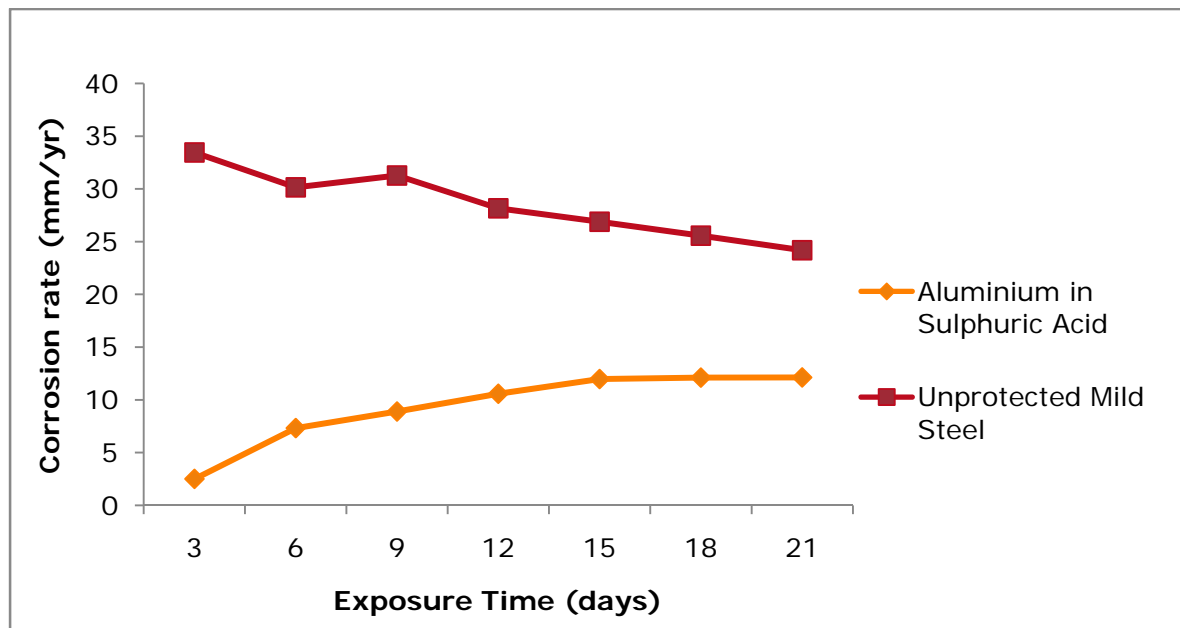


Fig.8. Variation of corrosion rate of mild steel sample with exposure time immersed in sulphuric acid with and without aluminium anode protection.

Potential Measurements

The results obtained for the potential measurement of the mild steel test specimens protected by zinc anode in seawater and in 0.2M H_2SO_4 are presented in Figs. 9 and 10 respectively. For mild steel test specimen protected by zinc anode in seawater, electrode potential values obtained decreased steadily from -725mV to -759mV after 21days as shown in Fig. 9. This result indicates that the mild steel corroded as a result of current flow in the aqueous medium used, thereby resulting in a decrease in electrode potential of the cathodically protected samples in seawater. The mild steel test specimen that was protected with aluminium anode, Fig. 9, was observed to be effectively protected. The potential of the cathode (mild steel) increased positively and progressively from -739mV to -715mV after 27days of exposure in seawater environment.

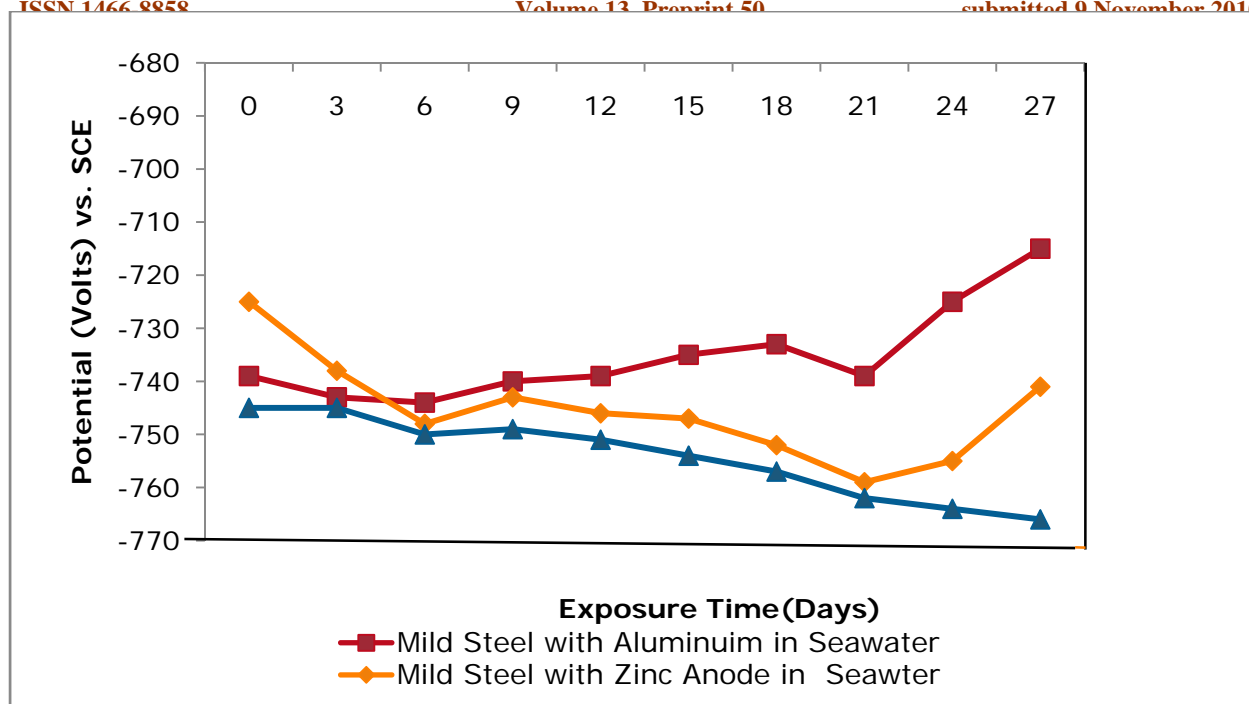


Fig.9. Variation of potential with exposure time for mild steel specimen in seawater

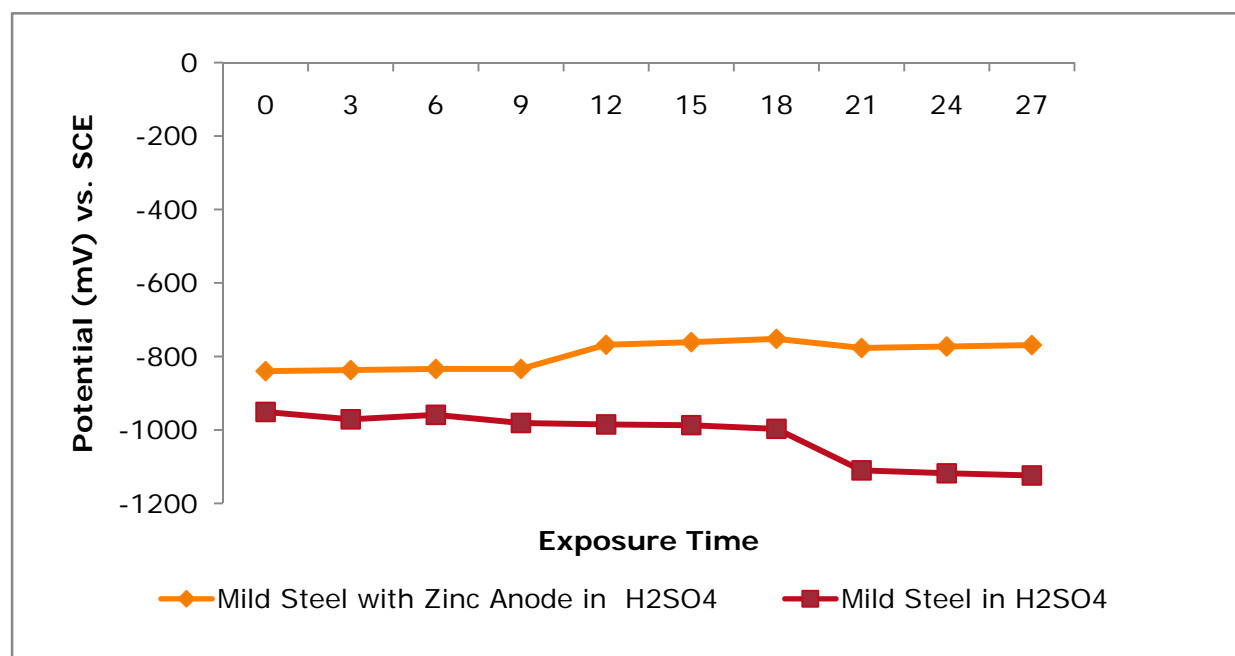


Fig.10. Variation of potential with exposure time for mild steel specimen in sulphuric acid.

In Fig.10, the zinc anode that was connected to the steel test specimen achieved a potential value of -800mV at the end of the experimental period. Similar test performed with the aluminium anode achieved a potential value of -1100mV at the end of the experimental period on the 27th day. These potential measurement results correlated with the results obtained in the weight loss method. The zinc anode appeared to be more effective in protecting steel in sulphuric acid than the aluminium.

In general, as previously mentioned, galvanic anodes are designed and selected to have a more “active” voltage - that is, technically having more negative electrochemical potential than the metal of the structure/component, usually steel. Mechanistically, for effective cathodic protection, CP, the potential of the steel surface is polarised (pushed) to more negative until the surface has a uniform potential. At this stage, the driving force for the corrosion reaction is halted. The galvanic or sacrificial anode continues to corrode and thus consuming the anode material until eventually it is replaced. The polarisation is caused by the current flow from the anode to the cathode. The driving force for the CP current flow is the difference in electrochemical potential between the anode and the cathode (the steel being protected).

CONCLUSION

1. Aluminium sacrificial anode is more protective cathodically for mild steel cathode in seawater environment.
2. Zinc sacrificial anode is also protective for mild steel in seawater, however, its rate of dissolution by corrosion is significant.
3. In the 0.2M H₂SO₄, the zinc sacrificial anode was found to be protective for the mild steel test specimen. It can, therefore, be used effectively for the cathodic protection of steel in this environment at the ambient temperature.
4. Aluminium sacrificial anode did not perform well in protecting mild steel in the sulphuric acid medium used. It can hence be concluded that it is not desirable to use it for steel protection in the sulphuric acid environment.

5. The different sizes of the zinc anode used confirmed that the effective cathodic protection performance of the anode also depends on its size. The bigger the anode, the more the electrons supplied to protect the cathode and the longer time it takes for replacement.

Acknowledgement

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