

Justification and Judgement to Corrosion Issues for Anode Selections on Navy ships

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Abstract

Sacrificial anodes have become an utmost technique to protect the exterior hull, stern drives and outboard parts of the ship. For many decades, zinc anode has become commonly used in cathodic protection devices as sacrificial anodes since it has been the easiest and cheapest material to be used and has done a decent job in most natural applications of seawater. Due to its elevated theoretical present effectiveness and low active potential, aluminium appeared as an exciting metal to replace zinc in the cathodic protection scheme. In this research, the performance of zinc alloy and aluminium alloy (will be mentioned as Al and Zn) as an anode to cathodic protection was assessed at distinct temperatures (20°C and 40°C) on the marine structure plate or ship's hull which made by carbon steel in natural seawater. Wavelength dispersion X-ray fluorescence spectrometry (WDXRF) has been used to evaluate the composition of the Al and structure plate (carbon steel) whereas atomic absorption spectrometer (AAS) and X-ray diffraction spectrometer (XRD) were used to assess the composition of a Zn and natural seawater. The magnitude of corrosion protection was determined by weight loss (immersion testing) and electrochemical by cyclic polarisation potential (CPP) technique. It has been observed that the weight loss of Zn is higher than Al after 4 weeks immersed in natural seawater at 20°C and 40°C. Similarly, the electrochemical data by CPP showing Al to have better corrosion resistance than Zn alloy due to instant oxidation and resistance to dealloying process. Overall results show that Al alloy has better performance than Zn alloy as sacrificial anode for cathodic protection in seawater. The potential of Al alloy is higher than Zn alloy on marine structure plate (carbon steel) in natural seawater, thereby becoming preferable protective cathode. Both anode materials show to have potential between -800mV to -900mV showing best galvanic potential over steel plate to be protected.

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Introduction

Cathodic protection (CP) a term given by galvanic method to protect metal structure especially carbon steel where the electrolyte exists. Galvanic cathodic protection (GCP)

or sacrificial anode cathodic protection is a system use electric current applied by the employment of dissimilar metals. The first application of cathodic protection and statement of the principles of the technique were made by Sir Humphrey Davy in 1824. Using small buttons of zinc, or iron nails,

attached to the protective copper sheathing installed on the hulls of wooden warships and he was able to arrest the rapid decay of copper [1]. Cathodic protection can only be applied when the metal is exposed to an electrolytically conducting environment. The driving voltage is created by the potential generated between the steel and the anode in the electrolyte. The only galvanic anodes used are alloys of Mg, Zn and Al [2-9], which can be applied to protect steel in aqueous and soil environments. Protecting any metal structure with cathodic protection from the corrosive environment can ensure cost efficiency throughout its lifecycle. Many studies have been carried out to use aluminium as an alternative in the cathodic protection system as a sacrificial anode, particularly since the 1960s when it became a common choice to safeguard steel structure from corrosion [1-3].

Results from this research will justify the efficiency of aluminium compared to Zn as sacrificial anode in CP. In any construction, replacing sacrificial anode might need experiment supporting data to satisfy the decision maker in upgrading materials. For military unit such as Royal Malaysian Navy (RMN) ships' underwater hull requires supporting performance comparison information between Zn and Al anode to replace existing Zn alloy as sacrificial anode for underwater hull. The supporting performance requires comparison information in defending the underwater hull of the vessels while at the jetty or sea. This is merely to prevent unnecessary increases in the danger of corrosion and possibly greater costs of mitigating the corrosion issue [4-5]. This study was conducted to identify and judge the most efficient anode material in protecting navy ships. It is including cost efficiency judgement including life cycle cost of upgrading sacrificial anode from Zn to Al in navy marine assets. The testing of

sacrificial anodes search for the following corrosion characteristics namely; breakdown potential E_b , open circuit potential OCP , passive range and corrosion rate from Tafel plot.

Therefore, conducting an academic study is crucial to determine powerful justification before the choice of whether or not to replace Zn with an Al anode. Any future changes will reflect important amounts of budgetary Ministry of Defense, so any choice to make those modifications will be backed by compelling information. It also needs adequate and cautious execution planning because anode replacement needs ships to be dry-docked and the vessel is deemed non-operational during the impacted period.

2. Experimental Procedure

Electrochemical testing was performed in a three electrodes cell providing an area of 2.25cm with a platinum counter electrode and silver/silver chloride (Ag/AgCl) as a reference electrode. Hydrogen evolution is the primary cathodic reaction taking place at these local cells. Thus, the measurement affords an indirect determination of the loss of efficiency of the anode. NACE TM0190-98 is based in one of these tests [6]. To study the sacrificial rate (corrosion rate) comparison in a real implementation, the cathode material was acquired from the ship hull and zinc anode was removed from the actual sample used on the vessel while aluminium anode was supplied from the local supplier. The natural seawater was taken from Lumut, Perak located on the west coast of Peninsular Malaysia. The natural seawater was assessed on its total dissolved solids (TDS) meter and pH. The chemical composition of both anodes is shown in Table 1.

Table 1 – Chemical composition of zinc and aluminium anode analyzed by atomic absorption spectrometry (AAS) and wavelength dispersive x-ray fluorescence spectrometer

Metal	Composition (wt. %)								
	Cd	Cu	Fe	Pb	Sn	Mg	Ni	Al	Zn
Zn	0.333	0.005	0.13	0.12	-	-	-	2.525	Bal.
Al	-	0.005	0.098	-	1.38	1.178	0.006	Bal.	5.16

Anodes and cathode coupons were first cut in square shape of 1.5 cm × 1.5 cm (exposed surface area of 2.25 cm²). A wire to be connected to the specimens before embedded in epoxy specimen mounting resins and hardeners as shown in figure 1 worked as working electrode (WE) in electrochemical test. The tests were started at the range of ±250 mV between cathodic to anodic potential with the scanning rate of 0.25 mA/sec.



Figure 1. WE embedded in epoxy with exposed area of 2.25cm²

2.1 Weight loss measurement by immersion test

The coupons were grounded to mirror image till 1500 grades, degreased and washed with acetone then finally rinsed with distilled water. 2 sets of galvanic couple namely aluminium coupled with structure plate made by carbon steel (Al-CS) and and zinc coupled with structure plate made by carbon steel (Zn-CS) have been prepared in two separate beakers. Beaker was filled with natural seawater such that the coupons are fully immersed. The salinity and pH were

3.65 and 7.6 respectively. Two sets of water baths have been used in achieving the seawater temperature of 40°C and 20°C. All anodes and cathodes were immersed in the form of facing each other with a separation distance of 7cm.

The duration of immersion testing was 4 weeks. The weight loss of each coupon was measured and recorded every on the day seventh. The corrosion product to be removed following NACE TM0169. All coupons were cleaned by a light scrub then followed by degreased and washed with acetone and finally rinsed with distilled water. The corrosion rate of each tested coupons are calculated based on the equation stipulated in ASTM G1-03.

2.2 Electrochemical by cyclic polarization potential (CPP) and Tafel

Electrochemical was conducted by using Wonatech Instrument model WPG100 Potentiostat/Galvanostat which controlled by WPCIPG Version 1.0 in conjunction with three electrodes namely; platinum as counter electrode, Ag/AgCl as reference electrode and coupons (Al, Zn, Al-CS and Zn-CS) as working electrodes in separate electrochemistry set-up. Natural seawater collected from Lumut, Perak coast as an electrolyte will experimentally differentiate with other electrolytes (3.5% NaCl) .

3. Results and Discussion

3.1 Weight loss and corrosion rate

Presently, the most commonly employed sacrificial metals for cathodic protection

systems are alloys of magnesium (Mg), zinc (Zn) and aluminium (Al). However, not all materials suitable in every environment. Therefore, this research was constructed to justify the efficiency applications of Zn compared to Al as sacrificial anode in cathodic protection technique. Weight loss measurement in immersion to revealed the metal reduction in time. Samples were cut into identified area (coupons) and reduction weight was calculated in duration specified. In general, as illustrated in figure 2, all coupons showed continuous weight loss over the specified exposure time. Al and Al-CS

shows drastically increased in weight loss in 2 weeks of immersion whereby Zn and Zn-CS shows rising in weight loss from starts till the end of immersion. It can be concluded that the weight loss will become higher as the time of immersion increased. However, it can be predicted the weight loss of Al and Al-CS will have constant weight loss as the time of immersion increased. After 21 days of immersion, Zn-CS showed the highest weight loss with 0.13 g while Al-CS loss by 0.1 g. The amount of weight loss were then converted to corrosion rate comply to ASTM G1-03.

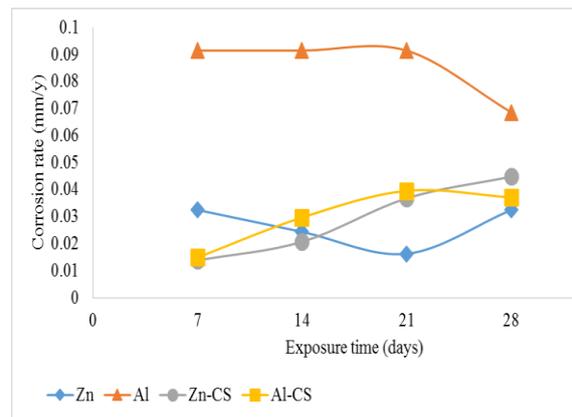
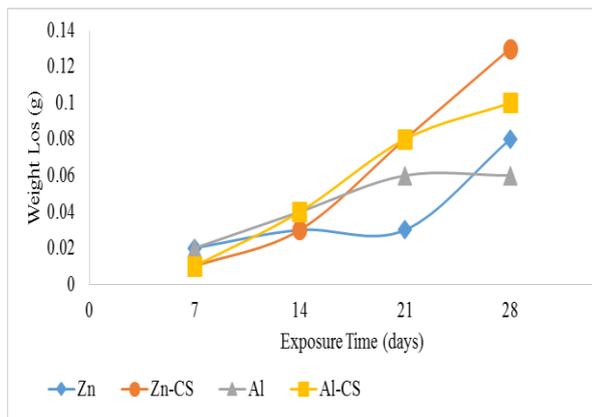


Figure 2 Graph weight loss (left) and corrosion rate (right) of different materials as a function of time in 20°C natural seawater

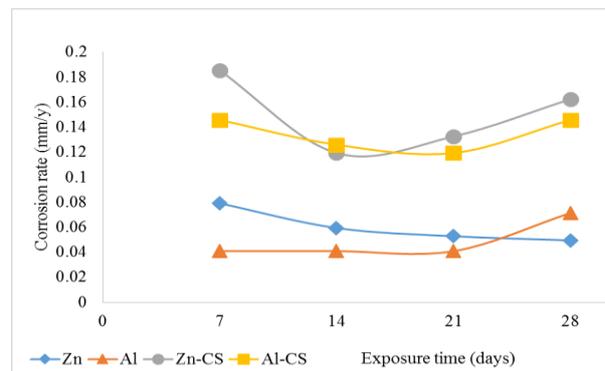
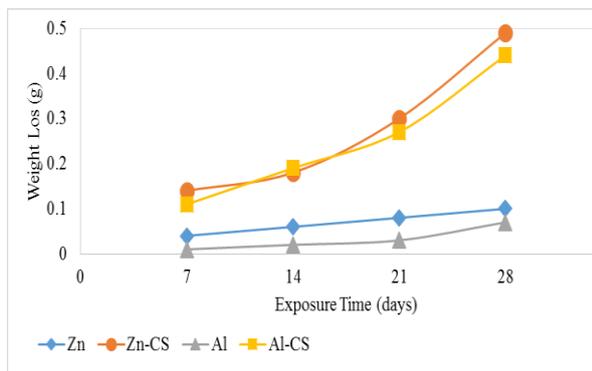


Figure 3. Graph weight loss (left) and corrosion rate (right) of different materials as a function of time in 40°C natural seawater

Constant weight loss revealed passive film developed on Al surface act as protection on metal surface which will slowly the electrochemical reactions and might effect of efficiency of Al as anode

protection. Al_2O_3 and $AlO(OH)$ are most likely corrosion products. From the results, it was revealed that the corrosion rate of aluminum did not provide a credible foundation on which aluminum anode

became more underwater boats and ships protection than zinc anode could provide [7-12]. However, higher rates revealed Al and Al-CS actively passivated to be oxide layer which means Al has immediate reactions compared to Zn and Zn-CS in corrosive media. Apart from local cell action, another reason for the loss of anode efficiency is a mechanical loss, i.e. physical detachment of metal from the anode [13].

Figure 3 revealed after 4 weeks immersed in the natural seawater at 40°C, Zn has loss of 0.1 g which is higher by 0.03 g of Al. Dezincification might be one of factors of corrosion attack. Zn-CS has weight loss of 0.49 g compared to 0.44 g of weight loss of Al-CS due to galvanic effect which the potential difference of Fe-Zn is higher than Fe-Al. From the curve, it is clearly seen that the Al-CS experienced lower corrosion reactions in Lumut, Perak natural seawater at 40°C than Zn-CS. It was also shown the consistency between weight loss and corrosion rate data compared to Zn with the effective Al corrosion protection of the cathode structure. The carbon steel weight loss could be ascribed against the corrosion attack at the area which was not layered but the corrosion product [6-14].

When placed in the natural seawater, aluminum will form a passive oxide layer. However, in the condition of the surface of metals, this passive layer is very dependent on the structure. The existence of distinct aluminum alloy phases could result in a micro galvanic corrosion between phases. The nobler stage is immune as the active site corrodes and leaves a material pitting. This condition may lead from disturbance of the formation of passive film [16]. The aluminum alloy's component may require the process of dissolution-precipitation and should achieve a critical value with the grain boundary leading to corrosion. Therefore, it is anticipated that the oxide film will dissolve and that a new film will appear at a much reduced pace [17].

Overall, corrosion rate increased as the electrolyte temperature increased. The rate of corrosion may also reduce at greater

temperatures, likely because it reduces the solubility of oxygen that becomes the variable. Lower in corrosion rate of the carbon steel as referred on the immersion testing results were due to the reality that building up corrosion products (passive surface film) may restricted oxygen transport to the surface, increasing surface roughness that improves momentum and mass transportation between surface and natural seawater. Nevertheless, the lower in corrosion rate was due to the increase in the diffusion rate of oxygen and enhancing the corrosion rate [18-20].

3.2 Electrochemical analysis

Parameters from Polarization (Tafel) plots has been analyzed. The polarization curves of different materials and the polarization curves of carbon steel in combination with either aluminum anode or zinc anode were shown in figure 4. The corrosion current (I_{corr}) was used to determine corresponding corrosion rate. The corrosion rate was manually calculated using expression as stipulated in ASTM G102-89. From polarization curves, it was shown that the formation of deposits resulted in decreasing current densities over time. As scales form, they act as a physical barrier and offer protection against further corrosion. Thicker and more compact deposits provide better coverage and, therefore, protect the steel more efficiently. The use of electrochemical techniques such as OCP and LPR over the test duration provided data describing the evolution of the system. Potential changes over the first few days showed the polarization of the exposed steel when there are less corrosion product generates by sacrificial anode activities. During these initial stages, air-formed oxides dissolved and new oxides/hydroxides of aluminium formed.

In figure 4 and Table 2, the corrosion potential of aluminum anode was -1107.6 mV. A smaller anodic curve might explain that in natural seawater aluminum is aggressive. The -1003.8 mV potential suggested an active dissolution of zinc in

natural seawater. The anodic and passivation current of carbon steel were the highest. The value of corrosion current was also the highest while the corrosion potential was the least. The higher anodic current for carbon steel indicated that it suffers more corrosion through its dissolution into ferrous and ferric

cations [21-23]. Figure 5 shows comparison of cyclic polarisation potential (CPP) of Zn and Al as sacrificial anode. Breakdown potential (E_b) and open circuit potential (OCP) of Al was higher than Zn suggested Zn to have better corrosion resistance as sacrificial anode in cathodic protection [18].

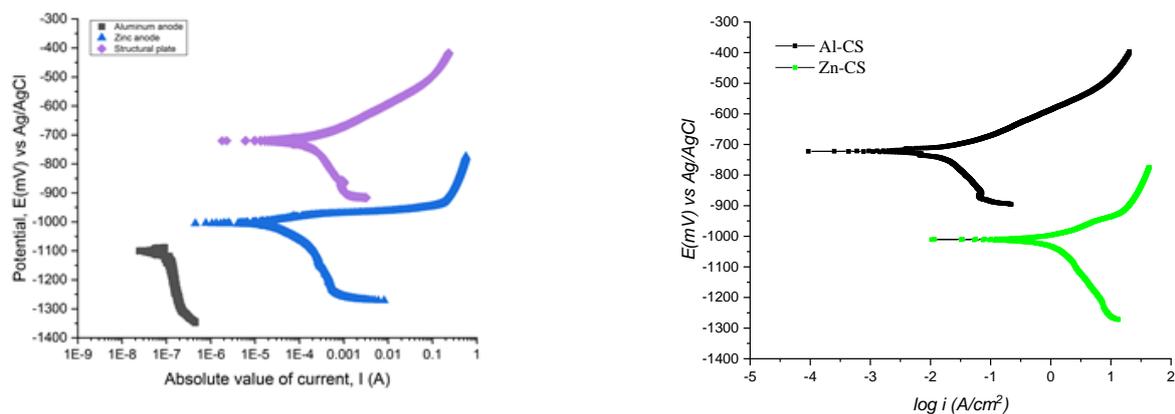


Figure 4. Tafel plot for anodes (left) and coupled anodes (right) in natural seawater

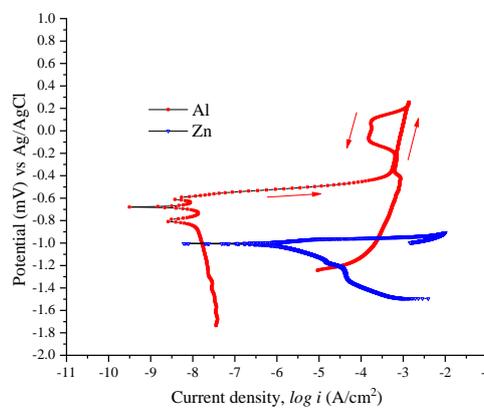


Figure 5. Cyclic potential polarization (CPP) for Al and Zn

Table 2. Electrochemical parameters

Material	E_{corr} (mV)	I_{corr} (μ A)	CR (mm/y)
Al	-1107.6	0.060721	0.2919×10^{-3}
Zn	-1003.8	1.8033	11.9897×10^{-3}
CS	-719.39	8.8341	46.1731×10^{-3}
Al-CS	-721.9	9.6647	0.046
Zn-CS	-1010.1	1580	1.18

3.3 Microscopy analysis

Microscopy analysis was performed to reveal the properties of corrosion product as a surface barrier on anodes material as shown in figure 6. The efficiency of corrosion

product as corrosion protection will determine the efficiency of CP system. Corrosion product on Al revealed oxide layer (Al_2O_3) which react as corrosion protection and delayed the corrosion attack [11].

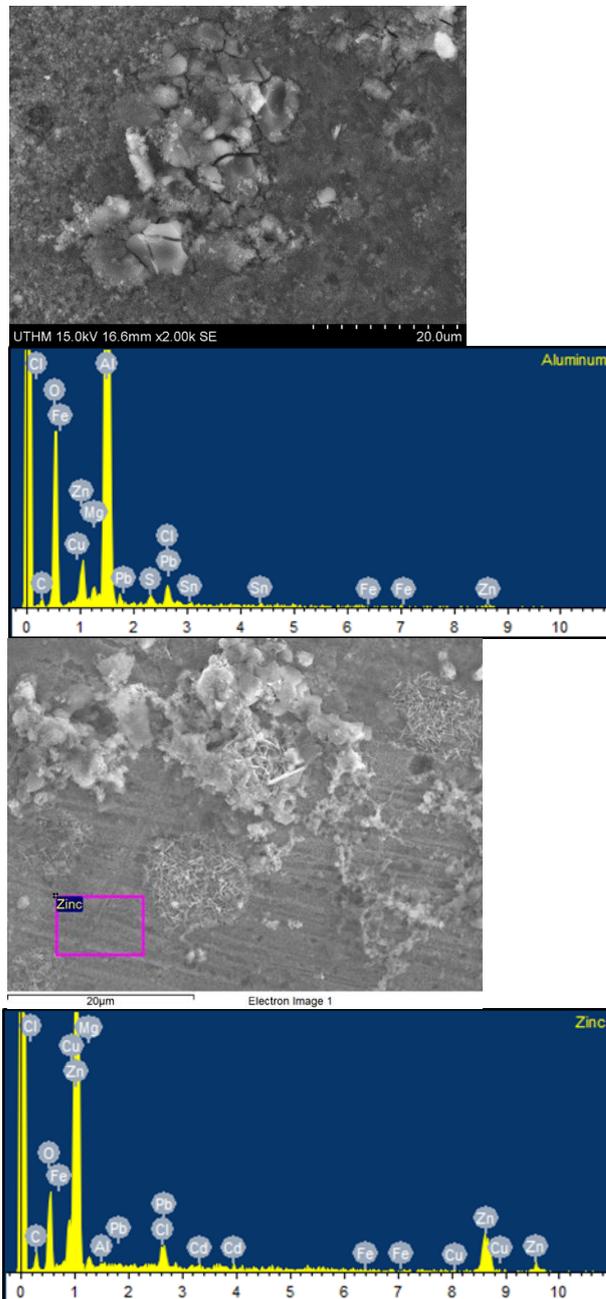


Figure 6. Microscopy and elementary analysis of Al (top) and Zn (bottom) after CPP test

4. Conclusion

Aluminium has attained considerable merit as the basis for a galvanic anode mainly due to its low density, large electrochemical equivalent, availability and

reasonable cost. Al-anodes are readily adaptable to a variety of saline environments such as seawater, marine muds and brackish waters. Nevertheless, the success of the Al-anode depends upon the alloying of certain

Element	Weight%	Atomic%
C K	6.66	11.80
O K	32.65	43.41
Mg K	0.49	0.43
Al K	51.54	40.63
S K	1.02	0.67
Cl K	2.29	1.37
Fe K	-0.23	-0.09
Cu L	0.66	0.22
Zn L	4.72	1.53
Sn L	0.08	0.01
Pb M	0.12	0.01
Totals	100.00	

Element	Weight%	Atomic%
C K	11.06	30.21
O K	14.63	30.00
Mg K	1.73	2.33
Al K	0.24	0.29
Cl K	2.68	2.48
Fe K	0.05	0.03
Cu L	-0.35	-0.18
Zn L	69.01	34.63
Cd L	0.40	0.12
Pb M	0.55	0.09
Totals	100.00	

metals whose surface role is to ultimately prevent the formation of a continuous adherent and protective oxide film on the alloy, thus permitting continuous galvanic activity of the Aluminium. Zn alloy as an anode has potential to be selectively attack by seawater with dezincification. Aluminum and zinc anode suitable to be used in marine applications (ships' hull). Nevertheless, aluminum anodes have reliable long term performance, and also have better current and weight characteristics than zinc anodes.

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