Performance of Aluminium Anode by Addition of Zinc in Sea Water – A Review

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Abstract: The main aim of this paper is to review the performance of aluminium-based sacrificial anode in the effect of zinc addition in sea water. The performance of aluminium anode is largely dependent on alloy composition and a good understanding of the relationships between the metallurgy and the anodic response of the alloys. Recent Researches show that with certain metallic alloys added significantly improves anode life and reduce costs.

Keywords: aluminium anode, anode efficiency, metallic alloys

1. Introduction
Presently, the most commonly employed sacrificial metals for anodic protection systems are alloys of magnesium (Mg), zinc (Zn) and aluminium (Al) [1]. Aluminium alloys are normally used in protecting steel structures in seawater because of their better current conductivity and supply largest number of electrons for protection per unit mass. This is because it has the advantages of being simple to install, independent of a source of external electric power, suitable for localized protection and less liable to cause interaction on neighboring structures [2]. Aluminium anodes are readily adaptable to a variety of saline environments such as seawater, marine muds and brackish waters. The quest for better surface activation, slower metal dissolution, greater protective output current, longer anode life. The corrosion protection of marine equipments and offshore structures can be provided by sacrificial anodes [3].

The development of new alloys of zinc and aluminum which have vastly increased the electrical capacity as well as achieving improved reliability and more negative electrical potential which greatly improve their performance [4]. The employment of each of these alloying elements is used in order to shift aluminum towards sufficiently electronegative values and to produce more uniform attack morphology.

This research studied the effect of zinc in aluminium anode used in marine and offshore structures [5].

2. History of Aluminium Anodes
Cathodic protection was first described by Sir Humphrey Davy in a series of papers presented to the Royal Society in London in 1824. The first application was to the HMS samarang in 1824. Sacrificial Anode made from iron attached to the copper sheath of the hull below the waterline dramatically reduced the corrosion rate of the copper. However, a side effect of the catholic protection was to increase marine growth [6],[7]. Davy was assisted in his experiments by his pupil Michael Faraday, who continued his research after Davy's death. In 1834, Faraday discovered the quantitative connection between corrosion weight loss and electric current and thus laid the foundation for the future application of cathodic protection [8]. Thomas Edison experimented with impressed current cathodic protection on ships in 1890, but was unsuccessful due to the lack of a suitable current source and anode materials. It would be 100 years after Davy's experiment before cathodic protection was used widely on oil pipelines. Now a days aluminium anodes for marine service from electrochemical test are researched till date.

3. Effect of Zinc on Aluminium Anodes
Zinc is only present in aluminium casting alloys of 7XX series. Otherwise, zinc is present merely as an acceptable impurity element in many secondary (scrapbased) die casting alloys. As such, zinc is quite neutral; it neither enhances nor detracts from an alloy’s properties. [9]. ZHU Meijun, DING Dong-yan et al [10] Investigate the effect of Zn content on tensile and electrochemical properties of 3003 Alalloy. The effect of Zn addition on the microstructure, tensile properties and electrochemical properties of as-annealed 3003 Alalloy was investigated. It was found that high density precipitates are observed in the Zn-containing alloys and the alloy with 1.8% Zn addition also has rod-like precipitates. The alloy with 1.5% Zn addition has the highest ultimate tensile strength. M.C. Carroll, P.I. Gouma et al [11]. Studied effect of Zn addition on the grain boundry
precipitation and corrosion of Al. Stress corrosion cracking (SCC) concerns in aluminum alloys containing Mg levels greater than 3.5% have been largely attributed to the formation of the beta-phase (Al3Mg2) at grain boundaries. It has been demonstrated that the beta-phase need not be continuous in order to provide a path for crack propagation, but aging treatments, exposure to intermediate to high temperatures, and excessively corrosive environments can all contribute to early failure of Al-Mg alloys due to SCC. Proof of the presence of a corrosion-prone secondary phase can be demonstrated easily through exfoliation testing and the associated lining of grain boundaries, which can be confirmed optically. Additions of Zn to these Al-Mg alloys in levels of 1–2 wt% have been shown to be more SCC resistant due to the formation of a stable ternary Al-Mg-Zn phase, the π phase. Recent studies have shown that Al-5083 variants which contain even minor levels of Zn (0.68–0.70 wt%) perform much better during exfoliation testing. Zinc additions of 0.68–0.70 wt% to sensitized 5083-based Al-Mg-Mn alloys preclude the formation of b-phase precipitates, resulting instead in the formation of a chemically and structurally distinct Al-Mg-Zn t-phase at grain and subgrain boundaries. The t-phase appears to be more resistant to corrosion than the b-phase.

### 4. Compositions of Existing Aluminium Anodes

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<td>Cu: &lt;0.006</td>
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<td>Fe: &lt;0.1</td>
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<td>Hg: 0.02-0.05</td>
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<td>Si: 0.11-0.21</td>
<td>In: 0.014-0.020</td>
<td>In: &lt;0.005</td>
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<tr>
<td>Zn: 0.3-0.5</td>
<td>Si: 0.08 – 0.2</td>
<td>Mg: &lt;0.01</td>
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<td>Others: Each &lt;0.02</td>
<td>Sn: &lt;0.001</td>
<td>Mn: &lt;0.01</td>
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<td>Zn: 4.0-6.5</td>
<td>Ni: &lt;0.005</td>
<td>Si: &lt;0.1</td>
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<td>Sn: &lt;0.001</td>
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Table 1 shows composition of some anode alloys of aluminium, zinc and magnesium. Comparing these alloys based on current capacity, Galvalum I gives 264 Ah kg⁻¹. The US Navy conventional and low voltage aluminium alloy sacrificial anodes are qualified for least current capacity of 2535 and 1656 Ah kg⁻¹ respectively [12]. The advantage of the aluminium anodes over zinc is obvious. On general basis of anode current capacity and anode consumption rate, aluminium alloys have been preferred for steel SACP [13].

### 4.1. Aluminium Anodes Compositions Researched till Date (Source: [14])

WP = Working potential, OCP = Open circuit potential, SSCPP = Steady state critical pitting potential, PP = Pitting potential, CP = Coupled potential, FP = Free potential, CCP = Closed circuit potential.
Table 2. Aluminium Anode Compositions Researched Till Date (Source : [14])

5. Experimental Procedure

An Al–Zn (5 at %)–Mg (5 at %)–Li (0.1 at %) alloy was prepared with commercially available Al, Zn and Mg with purities of 99.98%. Li was used as a wire of 3.2 mm in diameter and 99.9% of purity with 4.5 mg cm$^{-3}$ of sodium (Na). From previous experiments, and to prevent losses of Mg, Zn and Li during the melting process of these alloys, the elements were placed in Al capsules. Initially, the Al was placed in an alumina/graphite-coated crucible and melted in a resistance furnace under an argon atmosphere. Once the Al was melted, the liquid bath was overheated 150 °C and the Al capsules containing Zn and Mg were added. The bath was stirred with argon for 10 min to obtain a uniform distribution of Zn and Mg. Immediately after this operation, the Al capsule containing Li was added to the liquid bath, which was stirred with a flux of argon for another 5 min, after which time the liquid alloy was poured into a copper mould of dimensions 8 × 8 × 50 cm. The top and bottom of the ingot were cut o. for chemical analysis, thus obtaining a nominal composition of Al–Zn (4.8 at %)–Mg (5.1 at %) and Li (0.09 at %).

A representative microstructure observed in the as cast ingot. It consisted of a-Al dendrites with sizes between 130 to 150 μm. In the interdendritic regions, the presence of eutectic and black spherical particles was...
observed. The eutectic showed a white colour with a maximum width of 10 lm, always following the contour of the dendritic arms. This eutectic, instead of presenting a platelet morphology such as has been reported [15], showed the presence of rows formed by grey spherical particles. A short-term electrochemical test [16] was performed on the Al–Zn–Mg–Li alloy anode, corresponding approximately to Al–5Zn–5Mg–0.1Li. Cubic anodes were machined from the ingot, thus eliminating the structure formed by direct contact with the mould wall. The samples were put in a specially designed electrochemical cell, leaving only the cross section area of 1 cm² exposed and connected anodically to a d.c. current source, the cathode of which was a sheet of carbon steel. All the specimens were polished with 1200 emery paper, then degreased in acetone, washed thoroughly in double distilled water and kept in a dessicator.

An accelerated electrochemical test was carried out to determine anode efficiency and working potential [17]. All potentials were measured relative to a saturated calomel reference electrode (SCE). Samples were held galvanostatically at different current densities. Each level was applied for a 24 h period. The total, duration of the test was 96 hours. During the test, the anode potential was determined and electrochemical impedance spectroscopy (EIS) measurements were made at the beginning and end of each current density level period (every 24 h). This revealed any tendencies to passivation. The test solution was aerated substitute ocean water with an initial pH of 8.3 according to ASTM D1141 [18]. Electrochemical impedance was conducted by using a Gamry CMS300 Instrument over a frequency range of 10kHz to 100 mHz (10 points per decade) superimposing a 10mV a.c. signal and interpreted in terms of equivalent circuit with frequency dependent components. The equipment was controlled with a PC running EIS software, also from Gamry. EIS measurements were used to monitor the corrosion process on the aluminium anode daily for the 96 test hours.

At the end of the test, the samples were removed, cleaned and weighed to obtain the weight loss. The anode Efficiency was obtained by calculating the total charge passed through the system, the weight loss of the anode specimen and the corresponding electrochemical equivalent.

6. Results and Discussion

The trend of the anode potential (open-circuit potential) against time when the experimental alloys are immersed in a 3% NaCl is reported. The alloy needs time to reach a steady potential. This potential ( unders mV vs SCE) is very close to the electrode potential reported by Barbucci et al. [15] and Foley and Trzaskoma [19], who used an aluminium alloy very similar to that used in this study in a chloride containing solution.

The calculated electrochemical efficiency [20], e. for the as-cast Al anode samples was 61.43%, corresponding to 1832 Ah kg⁻¹. The closed-circuit potentials measured were in the range 1.05 V vs SCE at 0 mA cm⁻² to 0.86 V vs SCE at 4.0 mA cm⁻². An active closed-circuit potential is desirable because a relatively noble potential could indicate the presence of passivation. Anodes must also possess high faradaic efficiency to prevent frequent anode replacement. The NACE [21] and DNV [20] tests specify that an Al anode should have a closed-circuit potential active to 1.0V vs SCE and an e between 2300 and 2700 Ah kg⁻¹. Then the anode analyzed met the potential criteria, but it exhibited only moderate efficiency. Theoretically, uniform anode dissolution will give maximum efficiency. Either secondary cathodic reaction on the same interface and/ or mechanical grain loss due to local macro or microcorrosion cells will reduce the anode efficiency [21]. In Al–Zn alloys, Zn tends to be rejected to interdendritic zones or grain boundaries. This effect is favoured by the cooling rate and the alloying element characteristics (lower melting point than aluminium). Under polarization, this local composition variation will favour the initiation and propagation of macro- and microlocal events (galvanic corrosion and pitting for example). These events are responsible for lowering anode efficiency by electrochemical or mechanical mass loss [21]. The low efficiencies shown by the studied anodes are similar to those obtained by Salinas et al. [21] for Al–5%Zn alloy. A possible explanation is that the main efficiency loss can be ascribed to the second reactions, since they are produced by the relatively highcontent of impurities, particularly Fe and Cu, that cause local cell action.

Another possible reason for the low efficiency of the anode alloys tested is the effect of the formation of corrosion products on the self-corrosion rate of the anode surface significantly affects the electrochemical efficiency of the material, as pointed out by the results by which it can be observed that the electrochemical behaviour (performance) of the Al anode alloy is strongly dependent on the formation of surface corrosion products. It summarizes the resistance of the corrosion product. It is a function of applied current density. It is clear that the increase in current density produces a decrease in the resistance value of the corrosion products, Rcp, formed on Al anode. This is probably due to the fact that a heavier and denser corrosion product forms at a higher current density, thus promoting the self-corrosion activity [22]. This seems to prove the effect of the formation of corrosion products on the self-corrosion rate of the anode. Several authors [23, 24] have shown a relation between the electrochemical efficiency of anode materials and the anodic current densities. The anodic current density is therefore a test parameter that should be given due consideration. On specimens without a
well-developed corrosion product, the self-corrosion rate will account for a relatively higher portion of the total mass loss at lower anodic current densities. On partly consumed anodes, where corrosion products have settled, the maintenance and development of the corrosion products will be more efficient at higher current densities than at lower current densities. Consequently, the self-corrosion rate due to a more corrosive environment beneath the corrosion product will be correspondingly higher at high anodic current density [22].

EIS measurements were performed during the DNV test. The shapes of the diagrams show significant differences. At high and medium frequencies two depressed capacitive loops are evident, probably due to the oxide and to the aluminium faradaic dissolution. At low frequencies an inductive loop is detected. These results are in agreement with those obtained by Barbucci et al. [25] and other authors, although in their research unalloyed aluminium was studied. The capacitive behavior at high and medium frequencies might be due to the oxide passive and the metal–oxide interface (the charge transfer processes, Al dissolution through the oxide layer), whereas for the inductive behaviour, an oxide–solution interface (oxygen ion ingress in the oxide layer) could be ascribed to the faradaic processes.

It is evident from the electrochemical impedance data. It shows that the current density condition plays a critical role on the resistive property of the corrosion products, suggesting a significant change on the corrosion product property formed on the Al anode. Dark grey corrosion products were formed. The surfacedissolution morphology exhibited a rough, pitted surface. The EIS diagrams showed evidence of both passivation and pitting. The lower electrochemical activity exhibited by the Al anode samples strongly suggests that secondary reactions may be the fundamental cause of this behavior. In our experiments, the EIS diagrams obtained at higher current densities show an inductive semicircle which may be attributed to pitting corrosion. The preferred dissolution morphology is general attack rather than pitting, since pitting attack has been correlated to less than optimal performance.

Galvanostatic polarization was applied to the anode after the test. Under these conditions, the actual activeelectrode area had already reached a steady state value. The polarization test was performed at the end of the short-term electrochemical test to determine the anode behaviour type. The anodic polarization behavior showed that the anode efficiency obtained at low current densities would be the same as that obtained at high current densities. These results consolidate the accelerated dissolution test performed.Formerly an argument against using the short-term electrochemical test stated that in the two-week [20] or four-day [21] test, only the outer 260 lm is consumed, whereas in the one-year test at least 0.5 cm penetration is achieved. Murray et al. [26] have obtained successful results by showing that the evaluation of both the aascastmaterial simultaneously with the cut surfaces (which are representative of the bulk material) makes the short-term test appear representative of the castanode long-term performance.

7. Conclusions and Remarks

The presence of a secondary phase strongly affects the electrochemical behaviour of the Al–Zn–Mg–Li alloys studied. A secondary reaction led to significant loss in current efficiency and was dependent on the microstructure of the Al anodes. EIS is a useful tool to study the dissolution behaviour of Al-alloy sacrificial anodes when subjected to cathodic protection. The development of a new generation of Aluminium anodes will be quite a daunting task, since the number of permutations of alloying additions is vast; it seems improbable that significant improvements in anode performance can be achieved from further trial-and-error procedures [27]. Rather, a fundamental understanding of the relationships between the anodic response of these alloys (related to the operating potential) and the metallurgy (related to the attack morphology and therefore the current capacity) is needed [27]. The use of metallic activators like Zn, Sn, Hg, In, Bi and Ga have been very well researched, with obvious advantages and limitations. The available literature show that while good activation is achieved, current capacities and anode efficiencies can still be improved upon. However, some of these metal activated anodes have also been shown to undergo pitting corrosion in chloride environments. Therefore further developments can be made with the use of nano synthesized materials and other possible renewable materials, which is the main thrust of this research as not much literature is available on their use.
8. References


