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*Review Article*

# Limitation of Aluminum Anode in Cathodic Protection Applications

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***Abstract*** *- The commonly employed method for Cathodic Protection (CP) is the sacrificial anode system. This method involves protecting the metallic structure by sacrificing other metals that are more reactive. In this process, electrons are transferred from the sacrificial metal (which has more negative potential) to the protected metallic structure (which has more positive potential) through corrosive electrolytes using a connecting conductor. An aluminum (Al) anode is a sacrificial anode made of aluminum. Al alloy anodes have been utilized for several decades, mostly in large cathodic protection projects such as ports, subsea structures, ship hulls, and piling installations. This was attributed to the superior performance of Al in comparison to zinc (Zn), which surpassed the cost difference in larger projects. Nevertheless, the electrochemical characteristics of Zn are regarded as more stable than theirs. This study aims to highlight the constraints of the Al anode under different environmental and application conditions and elucidate the potential risks associated with the utilization of this particular sacrificial anode. Furthermore, it could serve as a scientific reference for the selection of a galvanic anode system.*

***Keywords*** *- Corrosion, Cathodic Protection, Galvanic Anode, Aluminum Alloy.*

## 1. Introduction

Cathodic Protection (CP) is a technique to reduce the corrosion of a metal surface by making that surface the cathode of an electrochemical cell. The cathode in an electrochemical cell is the electrode where reduction (and no corrosion) occurs. Prior to applying cathodic protection, corroding structures will have both cathodic areas and anodic areas (those areas where corrosion is occurring). It follows, then, that if all anodic areas can be converted to cathodic areas, the entire structure will become a cathode, and corrosion will be eliminated. This can be achieved by direct current being forced onto all surfaces of the structure to be protected. This CP current shifts the potential of the structure in the active (negative) direction, resulting in a reduction in the corrosion rate of the metal. When the amount of current flowing is adjusted properly, it will overpower the corrosion current discharging from the anodic areas on the pipeline, and there will be a net current flow onto the pipe surface at these points. The entire surface then will be a cathode and the corrosion rate will be reduced. There are two CP methods for preventing the corrosion of steel: (1) Impressed Current Cathodic Protection (ICCP), which involves the application of an external current onto the steel in order to bring its potential to within a cathodic range, and (2) sacrificial cathodic protection, which attaches more active metal to steel, protecting it via galvanic corrosion. The more active metal or sacrificial anode is deliberately forced to corrode in order to prevent the steel from degradation. Generally, the type of sacrificial anodes used is Zn, Al and magnesium (Mg) anode. Al-based alloys are attractive as anodes in the CP of steels in seawater due to their low cost and high current capacity. The main disadvantage of Al as a sacrificial anode is its natural ability to form a very stable and passive oxide layer, which hinders corrosion of the metal itself and shifts the metal potential to less-active values. It should be noted that more consideration must be taken in which way they are utilized. This paper seeks to demonstrate the efficacy of the Al anodes in various environmental conditions, including high temperatures and low chloride applications. It aims to assess the effectiveness of Al anodes in the presence of Alternating Current (AC) stray current. Additionally, it aims to showcase the performance of Al anodes in enclosed compartment structures. The paper will also address operation and safety concerns related to the physical position of Al anodes for tank internal applications. Lastly, it will address the impact of Al anodes on the marine environment.

## 2. Al Anode Behavior

Pure Al cannot function as a galvanic anode because the formation of stable oxide films causes the electrochemical potential to shift to a very noble potential (passivation). However, adding activators to the alloy to disrupt the oxide film formation can maintain an active electrochemical potential for the Al alloy. Therefore, by proper alloying, we

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can use Al anodes to supply cathodic protection current. The Al alloy consists of a combination of Zn plus cadmium and indium to keep the anode active. The Al alloy experiences self-corrosion. Some formulations add manganese, silicon, or titanium to the alloy to optimize the balance between activation and self-corrosion. Al anodes generally require chloride ions in the electrolyte to function properly. As the quantity of chloride ions decreases below normal seawater concentrations, the current capacity of the anode decreases, and the anode potential becomes nobler. However, it is necessary also to consider various operating conditions in order to assess the performance of the Al anode in terms of its current capacity (i.e., efficiency) and anode potential. Additionally, the safety and environmental conditions that may impede the use of Al anodes must be taken into consideration.

### *2.1. Al Anode Performance in High Temperature Applications*

Numerous researchers have investigated the functionality of Al-Zn-In anodes at elevated temperatures and high applied current densities. The operating potential of Al-Zn-In anodes is positively shifted, and the current capacity decreases as the temperature of the electrolyte increases, as has been observed. As indicated in [1], the current capacity performance of the indium-activated anodes was 40% of the value obtained at an ambient temperature of 80°C. Furthermore, it has been proposed that the efficacy of Al–Zn–In anodes may have been compromised by an increase in self-corrosion. The behaviour of indium-activated Al alloys used as sacrificial anodes has been examined by Faghalyi and Scartleburg [2] in both field and laboratory experiments at temperatures spanning from 0° to 80°C. The current capacity and operating potential behaviour of the anodes were determined by conducting galvanostatic experiments on the as-received Al–Zn–In anode using the recommended NACE electrochemical test methodology [3]. On the Al-Zn-In anodes, tests were conducted for 2 and 4 weeks, accordingly, at low current densities of 0.05, 0.1, and 0.5 A/m$^2$. In the 2-week exposures, the test temperatures were 0°, 20°, 50°, and 80°C, while in the 4-week exposures, they were 20°, 50°, and 80°C. We conducted all of the experiments in a solution containing 3.5 wt. % NaCl. The data is presented in Table.1 demonstrates that with a rise in test temperature, the anodes' operating potential changed towards the electropositive direction, resulting in a decrease in current capacity. It is observed that the current capacity has increased in proportion to the increase in the applied current density. The test results indicate that at a temperature of 80°C, the average anode current capacities are 593, 119, and 53 Ah/kg at applied current densities of 0.5, 0.1, and 0.05 A/m$^2$, respectively. However, according to ISO-15589-2 [4] and DNVGL-RP-F103 [5] international standards, the anode current capacities at a temperature of 80°C for applications immersed in seawater are 900 and 720, respectively. It is evident that [4&5] standards offer valuable guidance when the anode current density is sufficiently high. However, if the anode current density is low, the anode current capacity may be lower than the published values in [4&5].

**Table 1. Electrochemical behavior of Al–Zn–In anodes exposed to different temperatures (20 to 80°C) [2]**

| Applied Current Density (A/m$^2$) | Applied Temperature (°C) | Average Current Capacity (Ah/kg) | Average Operating Potential vs. SCE (-mV) |
|---|---|---|---|
| 0.05 | 20 | 192 | 1105 |
| | 50 | 89 | 1056 |
| | 80 | 53 | 1038 |
| 0.1 | 20 | 518 | 1107 |
| | 50 | 455 | 1068 |
| | 80 | 119 | 1037 |
| 0.5 | 20 | 1421 | 1107 |
| | 50 | 861 | 1065 |
| | 80 | 593 | 1033 |

Several studies have investigated the corrosion morphology of Al-Zn-In anodes at different temperatures; Fischer [6] studied the effects of temperature and depth on the behavior of Al-Zn-In anodes in natural seawater. At ambient temperature and pressure, it has been observed an even distribution of pits over the anode surface. At higher temperatures, the corrosion morphology was much more irregular, with deep, large pits and grooves. In general, at higher temperatures, the corrosion morphology was more localized and increasing the pressure further localized the attack. In general, the corrosion morphology changes from uniform to very localized with increasing temperature.

Grant [7] conducted detailed research on the corrosion morphology of Al-Zn-In anodes at temperatures ranging from 20 to 80°C using various current densities (0.1, 0.6, 3, and 6 A/m$^2$). "The ideal attack morphology should be smooth and non-localized" at ambient temperature. The corrosion morphology at 0.1 A/m$^2$ indicates that the anode is active only on about 25% of the overall area, and the corrosion spreads outwards. Increasing the current density to 0.6 and then 3 A/m$^2$ expands the active area even further. At 6A/m$^2$, it appears that the entire surface was activated at some point during the test.

At higher temperatures, the test demonstrates that the corrosion morphology at a current density of 3A/m$^2$ and within the temperature range of 20 to 80°C, as depicted in Figure 1, was confined to a specific area. Furthermore, the affected areas exhibited a smooth surface at 20°C. It is worth noting that there was no adhesion of corrosion products. Raising the temperature to 40°C restricts the area of assault to vertical trenches. The trench effect is amplified at a temperature of 60°C. The ditches were coated with corrosion products, creating an outline that resembled the corrosion pattern. Raising the temperature to 80°C alters the corrosion

morphology once more. The attack manifested as numerous small cavities that appeared to erode the surface, with certain regions remaining inactive. This is distinct from a temperature of 20°C since the attack did not occur in smooth equi-penetration areas. It is also different from temperatures of 40 and 60°C, where the attack was localized to large deep pits. It was discovered that corrosion products surrounded the areas of activation.

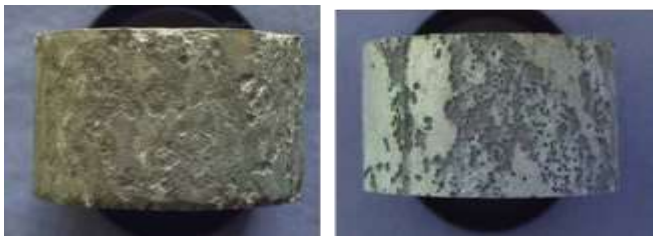

**Fig. 1 Corrosion morphology. Left: 20°C; Right: 80°C (current density: 3A/m$^2$) [7]**

### *2.2. Al Anode Performance in Low Chloride Application*

The performance of Al galvanic anodes mostly depends on many environmental factors, including temperature, pH, sulfate, and chloride content. These anodes are commonly utilized in seawater applications, while the passivation of Al anode is promoted in case of low chloride concentration and near neutrality pH in soil, which restrict their usage as galvanic anodes.The study, reported in [8], attempted to assess the effectiveness of Al galvanic anodes in modeling solutions with varying chloride and sulfate content. The objective was to examine their electrochemical behavior for potential practical applications. Figure 2 shows the results of free corrosion potential tests performed in sulfate-free solution with chloride concentrations of 300, 1,200, and 3,600 ppm during a one-year period. In general, the free corrosion potential of Al-Zn-In alloys decreases (going more negative) with increasing chloride concentration.

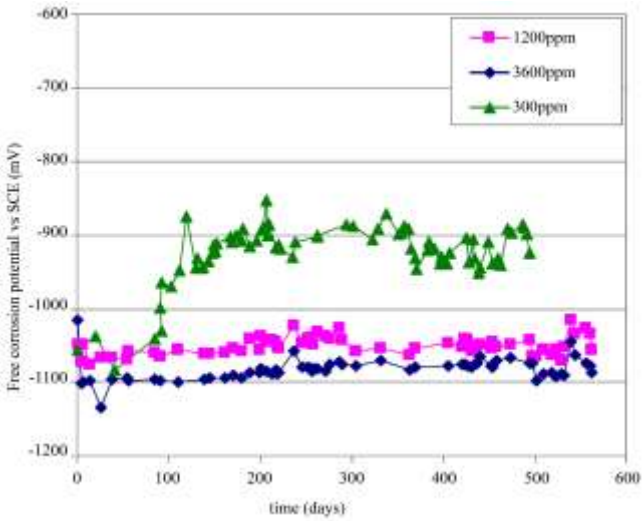


**Fig. 2 Free corrosion potential Ecorr trend for Al-Zn-In alloys (free sodium sulfate solution) [8]**

In order to ascertain the anode's working potential (pitting potential) in the presence of chloride and sulfate, potentio-dynamic experiments were implemented. Sulfate ions have been observed to have an inhibitory influence on the pitting-like corrosion behavior of Al-based anode alloys.

The pitting potential in relation to chloride and sulfate concentration has been examined, and it has been demonstrated that the anode's working potential decreases (becomes more negative) as the chloride/sulfate molar ratio increases. Additionally, it is observed that the concentration of chloride has a greater impact than that of sulfate. This is due to the fact that the anodes used were of the Al-Zn-In type, which is more susceptible to chloride than sulfate. Conversely, purified Al that lacks activation elements exhibits an opposite behavior, in which sulfate is more significant.

### *2.3. AL Anode Effectiveness in the Presence of AC Stray Current*

Hydrate formation is a well-known risk in subsea pipelines, and several solutions are available to solve this problem. Hydrates can be prevented by using Subsea pipeline electrical heating technology. Direct Electrical Heating (DEH) controls the temperature of the pipeline and is expected to be an efficient and convenient way to deal with wax plugs in the subsea pipeline. At the far-end cable connection point, the cable current enters the steel pipe, while part of the current (around 20-40 %) leaves the pipe and is transferred to the sea through the anodes. The electrical current in the sea water enters the pipe again at the near-end connection point. Sacrificial anodes shall prevent AC corrosion in the Current Transfer Zone (CTZ); in addition to providing an adequate CP system for the subsea pipeline, the anodes act as effective grounding for the pipeline. The use of this system is associated with drawbacks such as higher consumption of the sacrificial anodes of the CP system and the possible risk of AC corrosion of surrounding sacrificial anodes and the pipeline itself at coating defects [9]. Williams [10] reported a considerable increase in corrosion of Al conductors in water when an alternating current was applied, the extent of which was dependent on time and applied AC level. Corrosion occurred mainly during the initial test period and the corrosion rate increased with applied AC in the test range of 50 A/m$^2$ to 2000 A/m$^2$. In addition, Forthun [11] focused on studying further the effect of AC on the corrosion of Al-Zn-In anodes, both in the presence and absence of connection to steel. In this regard, different test configurations were employed, i.e. a pair of coupled anodes (A/A experiments) and steel coupled to anode, which in turn was coupled to another identical pair of parallel-coupled anode and steel sample (SA/AS experiments). In both cases, a constant AC density was applied, and experiments were designated by the current density level that was applied (relative to the area of one anode sample and assuming the overall current was transferred only between anode samples).

Figure 3 demonstrates that there is a noticeable rise in anode corrosion rates as the applied AC level increases in both A/A and SA/AS tests. This trend continues until the applied AC level reaches iac 80-90 A/m$^2$, after which the corrosion rates start decreasing with any additional increase in the applied AC level. Observations from high AC level testing showed that the test solution experienced heat generation and increased thickness due to the creation of extreme quantities of corrosion products. Replicates were conducted at a current density of 10 A/m$^2$. In the SA/AS experiments at this AC level, only one of the anodes exhibited corrosion. The extent of corrosion seen was similar to the combined corrosion rate of both anodes in the A/A experiments.

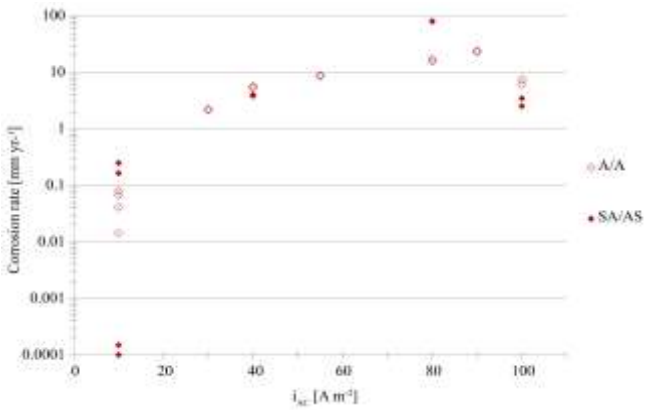


**Fig. 3 Anode corrosion rates in SA/AS and A/A experiments as a function of applied AC level [A/ m$^2$] [11]**

Figure 4 explained that when comparing tests conducted at the same Alternating Current (AC) level, there were no discernible variations between the anodes from the A/A and SA/AS experiments. In other words, the anodes' appearance was not significantly impacted by their connection to steel. The corroded surfaces exhibited an irregularly dispersed form of deterioration. The formation of pits expanded in both extent and size and further merged together as the level of Alternating Current (AC) increased correspondingly. The study reported in [11] clarified that the application of AC did not significantly affect the resulting anode efficiencies (standalone Al alloy) when low AC voltage was applied; however, it was observed that at 2 V AC and higher, the anode capacity (and resulting current efficiency) was lower than the acceptance criteria set by DNV-B-401 [12] for testing the anode capacity of Al-based anodes (i.e., 2500 Ah/kg). In addition, Thorsteinsen [13] investigated the behavior of Al-Zn-In sacrificial anode material in the presence of AC. The anode capacity can be determined from his findings. The anode capacities are significantly lower than the theoretical capacity, as illustrated in Figure 5 [14]. The anode current capacity is consistently less than 1000 Ah/kg, regardless of the varying AC current densities. These tests suggest that the introduction of AC results in a decrease in anode capacity.

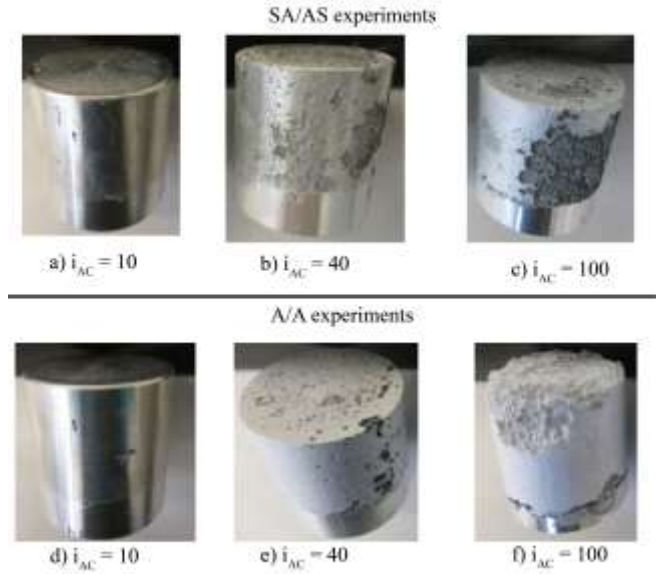


**Fig. 4 Clear variations in surface attack of anode samples after one week of AC testing at various AC levels [A /m$^2$] in SA/AS and A/A experiments [11]**

The author [9] conducts a thorough case study to assess the impaction of DEH on the CP system of an 11.5km subsea pipeline. The study highlights the necessary number of Al-Zn-In bracelet anodes needed to achieve the optimal level of protection in both the CTZ and the total length of the pipeline. This determination is based on the actual anode current capacity and corrosion rate, as demonstrated earlier. The conventional CP system only needed 40 anodes. However, in the case of both CP and DEH systems under worst-case conditions, up to 324 anodes were required (eight times the number of anodes needed in the conventional case). The results indicate that the DEH system significantly impacts both the CP design and the performance of the Al sacrificial anodes.

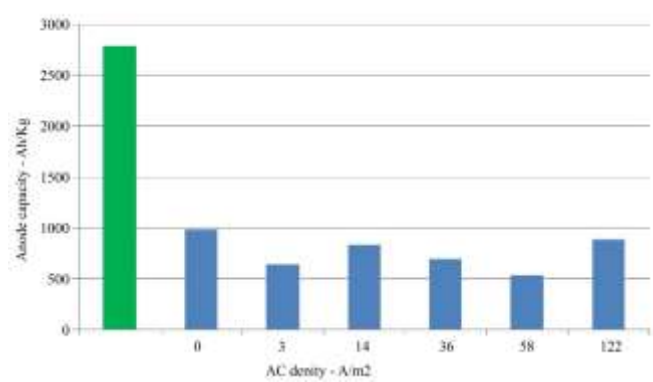


**Fig. 5 Calculated Anode Capacities at different AC current densities [14]**

### *2.4. AL Anode Effectiveness in Close Compartments*

There are many interacting factors which affect the cathodic current densities and changes in the water chemistry caused by the application of cathodic protection. CP is often

accomplished in enclosed compartments by the utilization of sacrificial anodes. Either Al or Zn is utilized, and current standards do not differentiate between the two. Al alloy anodes were chosen over Zn anodes mainly because they offered a better balance between weight and electrochemical capacity. Any decrease in anode weight that could be obtained was favored during installation. However, it is imperative to study the CP design parameters and the impact of sacrificial anodes on water chemistry, particularly pH, in enclosed spaces. The hydrolysis of the anode corrosion product is the sole method of introducing acid into the solution in sacrificial anode CP systems. $AlCl_3$ (Aluminum Chloride) is the primary corrosion product of Al anodes in seawater, and it can be hydrolyzed in water. Nevertheless, it has also been indicated that Aluminum Hydroxide is produced through the reaction between water and Al ions. As the acid is introduced, the concentration of Al ions increases, resulting in a decrease in the pH of the environment. Delwiche, Tavares & and Lydon [15] investigate the impact of the usage of Al anodes for cathodic protection in a stagnant water (close compartment) environment; it has been proven that Al sacrificial anodes will result in acidification of the seawater. The pH level will be reduced from ~8 to approximately 4.3 over a ten-week period, as presented in Table 2. Briskeby, M Hesjevik & L Borvik [16], comprehensive testing has been carried out to evaluate the CP design parameters such as anode capacity and design current densities and any effect sacrificial anodes, mainly Al-Zn-In and Zn anodes have on the water chemistry, especially pH. Furthermore, Figure 6 illustrates the surface appearances of anodes following testing. It has been established that the surfaces of Al anodes are characterized by local corrosion attacks, whereas the corrosion in the case of Zn anodes is much more uniformly distributed.

**Table 2. Calculated and measured pH values for different concentrations of $AlCl_3$ in Water [15]**

| $AlCl_3$ Concentration ppm | $Al_{3+}$ Concentration Moles $dm_{-3}$ | Calculated pH | Measured pH in Laboratory Trial |
|---|---|---|---|
| 0 | 0 | 7 | 7.6 |
| 5 | $7.59 \times 10^{-6}$ | 5.04 | 7.1 |
| 10 | $1.52 \times 10^{-5}$ | 4.89 | 6.1 |
| 20 | $3.04 \times 10^{-5}$ | 4.74 | 4.7 |
| 30 | $4.55 \times 10^{-5}$ | 4.65 | 4.5 |
| 100 | $1.52 \times 10^{-4}$ | 4.39 | 4.2 |
| 200 | $3.04 \times 10^{-4}$ | 4.24 | 3.9 |
| 300 | $4.55 \times 10^{-4}$ | 4.15 | Not Determined |
| 500 | $7.59 \times 10^{-4}$ | 4.04 | Not Determined |
| 1000 | $1.52 \times 10^{-3}$ | 3.89 | Not Determined |
| 2000 | $3.04 \times 10^{-3}$ | 3.74 | Not Determined |

**Fig. 6 Anode surface appearance after testing. Left: Al anode; Right: Zn anode [16]**

In this study [16], it was found that there is a major difference in the required current demand to achieve the optimum protection level that is dependent on sacrificial anode material. The main reason for the large difference in current density between testing with Al and Zn anodes is believed to be the acidification and pH difference. The mean current densities using Al anodes are in the high range and even, in some cases, above the recommendations given in [12].

Testing with Zn, on the other hand, shows much lower current density values than recommended, as Zn sacrificial anodes do not lead to acidification of the seawater. Figure 7 presents the predicted anode mass in relation to the design life. Based on the given anode geometry and the difference in anode capacities, opting for Al would need a smaller amount of anode mass throughout the initial 10-year period. Design life Zn anodes grow more advantageous from 10 years to 25 years. Zn has a higher density than Al, which will lead to a significantly lower number of anodes being installed.

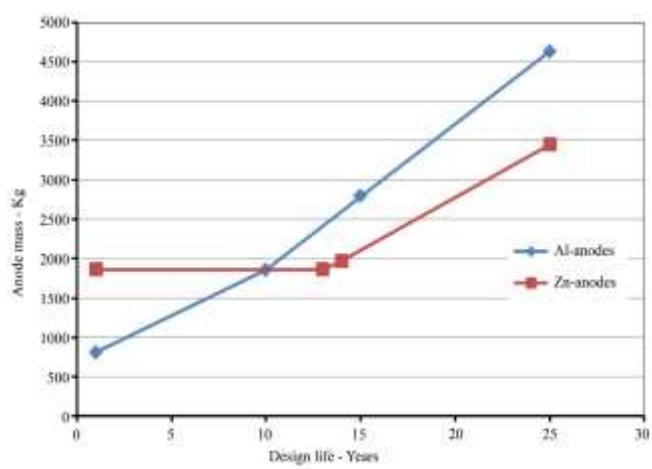


**Fig. 7 Anode mass calculations with respect to design life [16]**

### *2.5. Operation and Safety Restrictions of AL Anode Utilization in Tank Internals*

Sacrificial anodes have become a standard practice for the protection of ballast/water tanks against corrosive damage. Sacrificial anodes only become effective when fully immersed in an electrolyte for a longer period of time. In practice, however, ballast tanks are filled or emptied in function of the quantity and distribution of the cargo on board. Expected sea state and condition, together with the weather forecast, will also influence the quantity of ballast on board. Ballast or water tanks are not necessarily filled for 100 %, leaving a void space above the seawater. It is a standard rule not to fill up the ballast tanks completely to prevent overflowing tanks.

Al-Zn-In alloy anode has good electrochemical properties when continually immersed in seawater. However, the performance of the anode decreases in the cyclic immersion conditions, with the working potential shifting positively and the capacity and current efficiency lowered. Xu, Ma, Li & Wang [17] performed a detailed cyclic immersion tests with a variation of the immersion ratio of the anode. The immersion ratio is defined as the immersion time divided by the total period of testing in a wet/dry cycle. In condition I, the anode was immersed in seawater for one day, followed by exposure to the air for three days in a cycle. In condition II, the immersion ratio was 50%, with one day of immersion in seawater and one day in the air as a complete cycle. Condition III had the same immersion ratio as condition I, but the immersion period and exposure time in the air were 2.5 and 7.5 days, respectively. Condition IV was similar to condition I, while the anode was not exposed to the air but in a salt fog cabinet.

The anode tested under condition II exhibits a higher capacity and efficiency than the anodes tested under other cyclic immersion conditions. This indication suggests that a high immersion ratio can enhance the anode's performance. Condition III exhibits the same immersion ratio as condition I, but it has extended cycles of immersion time and exposure time in the atmosphere, as shown in Table 3. In contrast to the anode in condition I, the anode tested in condition III exhibited superior electrochemical properties and a more negative working potential, as illustrated in Figure 8. This implies that the anode's performance under cyclic immersion conditions is enhanced by prolonged immersion in seawater and a reduced number of total wet/dry cycles.

**Table 3. Practical Capacity and Current Efficiency of Al-Zn-In Alloy Anode under Different Testing Conditions [17].**

| Testing Condition | Full Immersion | I | II | III | IV |
|---|---|---|---|---|---|
| Capacity / A.h/kg | 2552 | 2097 | 2321 | 2185 | 1941 |
| Efficiency / % | 88.6 | 72.8 | 80.5 | 75.8 | 67.3 |

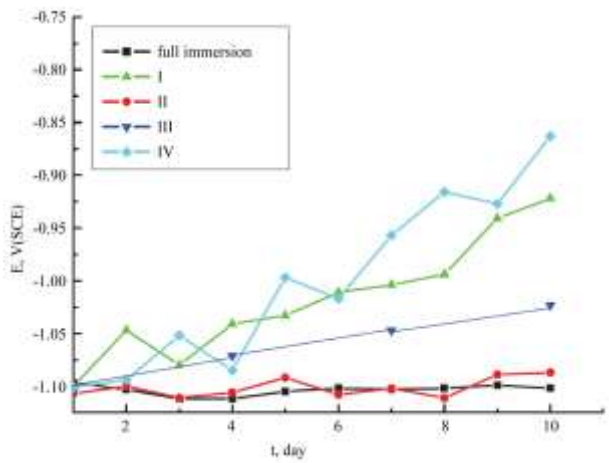


**Fig. 8 Change of working potential of Al-Zn-In alloy anode in seawater under different immersion testing conditions [17]**

Condition IV is the most severe of all the testing conditions, and the anode exhibits the lowest performance. The anode that is exposed to the salt fog atmosphere with high humidity experiences the most rapid self-corrosion. The surface of the anode is covered by the corrosion product that is produced during corrosion in the salt fog cabinet, and it adheres firmly. This leads to severe corrosion in the local area. The local corrosion and the mass loss from atmospheric corrosion in the fog cabinet are undoubtedly responsible for the reduced capacity and efficiency.

It is important to mention that the anode's appearance with corrosion products was detected following the electrochemical properties testing [17]. In the context of comprehensive immersion testing, the anode exhibits a consistent look with minimal accumulation of corrosion byproducts on its surface. During cyclic immersion testing, it is seen that some corrosion products stick to the surface of the anode. In particular, for the IV testing condition, the surface of the anode is nearly fully coated with corrosion products. The anode exhibits a highly homogeneous disintegration on its surface when fully immersed. During cyclic immersion, the remaining anodes exhibit a coarse texture characterized by small depressions. The anode, when examined under condition IV, exhibits significant localized corrosion, with certain areas of the surface remaining undissolved. Al anodes are generally preferred over Zn anodes as a result of their technical and economic advantages. However, there are safety concerns about using Al alloyed anodes in certain tanks due to the risk of sparking if the anodes fall off. The restrictions apply under the circumstances of the Tank for liquid cargo and/or crude oil with a flash point <60 °C or ballast/water tanks adjacent to tanks for liquid cargo with a flash point <60 °C. It is well stated [18] that Al alloy anodes in ballast tanks are to be so located in the tanks that a kinetic energy of ≤ 275 J is developed in case of their loosening and falling, which is in relation to the anode weight and height inside the tank.

### *2.6. Al Anode Impaction in Environments*

Al is one of the most abundant metals in soils and sediments and it makes up about 8.1% of the earth's crust, and it is normally not defined as a pollutant. It occurs in a range of solid phases, including aluminosilicates, aluminum oxides ($Al_2O_3$) and bauxite ($Al_2O_3.nH_2O$). At ambient earth surface pressures and temperatures, Al in the ionic form [$Al^{3+}$] is present as the aqua-complex [$Al\ (H_2O)_6^{3+}$] in water. Al is not clearly recognized as a toxic metal; however, several studies have reported neurotoxic reactions in animals during laboratory experiments. The chemical speciation of Al is likely to play a key factor in its potential bioavailability and toxicity [19]. Since the late 70's, the research range on the toxicity of Al has been extended to natural habitats, including forests and aquatic areas. The toxicity of Al is closely connected to pH levels. Metal is soluble under acidic conditions (pH < 5.5) in soil and water. It is also biodegradable. But it is relatively harmless under neutral conditions (pH 5.5 - 7.5) Reduction or death of invertebrates in forests and water, even the reproduction of fish and amphibians, are directly related to Al pollution. It also affects birds and mammals through the food chain indirectly. In the aquatic environment, Al acts as a toxic agent on gill-breathing animals such as fish and invertebrates.

In fish, the inorganic monomeric species of Al reduce the activities of gill enzymes important in the active uptake of ions [20]. Al alloy is the main material used as sacrificial anodes in seawater; Al anode metal will gradually dissolve and be released into the marine environment, protecting the structure against corrosion. Once the metal particles have been released, they may settle in the surrounding waters and affect the ecology. $Al^{3+}$ ions generated by anodic dissolution may co-precipitate with calcareous deposits, and they may result in hydrosulfate, which will possibly deposit into the final precipitate. The existence of Al in the acid-soluble portion of the sediment may have significant environmental influences. Hence, using Al sacrificial anodes in a natural environment, especially to protect the facilities near the coast, will increase the amount of deposited metals [21].

The toxicity of Al or Zn from either sacrificial anodes or from dissolving their sulfate salts was comprehensively investigated in [22]. Significant concentration-related toxicity was both exerted by Al and Zn sulfates, whereas no toxicity was detected by rearing embryos in sacrificial anode dissolved Al or Zn within the tested concentration range. The observed differences in toxicity outcomes between sacrificial anodes and sulfate salts administration both of Al and Zn held true for developmental abnormalities following embryo exposure as well as in the offspring of pretreated sperm; less clear-cut yet observed, this distinction also applied to sperm exposures in terms of fertilization success. It should be noted that a major question relating to Al and Zn speciation in seawater according to sacrificial anodes or sulfate salts dissolution is open to further investigations. It is well known that the concentration of free heavy metal ions is largely dependent on pH and Eh values as well as on the possibility of complication by various organic ligands. This is well documented for Zn and much less for Al.

## 3. Discussion

Generally, alloys used for galvanic anodes shall be based on Al, Mg and Zn. The performance, and therefore the suitability of a particular alloy for a specific application, will depend on the composition and characteristics of both the alloy and the electrolyte, the temperature of operation and the anode current density. The performance of a galvanic anode alloy is dependent on its actual chemical composition and homogeneity, current density and the environmental conditions to which it is exposed. The performance data shall include the current capacity in amp-hours per kilogram (A.h/kg) and the closed-circuit potential of a working anode measured against a standard reference electrode. Since the method of CP is electrochemical in nature, the anode material's electrochemical properties shall be determined under the expected environmental operating conditions. These may include the anode potential anode current capacity, in addition to the anode surface morphology which affects the efficiency and shall also be considered. The electrochemical properties of Al-based alloys vary depending on the specific alloy composition, operating temperature, operating anodic current density and the operating environment. The anode potential w.r.t Ag/AgCl seawater reference electrode is -1,09v, and the anode current capacity is 2500 A.h/kg [23] are the typical properties of Al anodes in normal operation (ambient temperature, normal seawater, anodic current density higher than 1 $A/m^2$). However, the corresponding values that shall be considered in the design are -1,05v and 2000 A.h/kg for the anode potential and anode current capacity, respectively [4, 5&12] in the same normal operation conditions.

The practical Al anode current capacity is different for anode materials exposed to different environmental conditions such as hot and cold electrolytes seabed mud, i.e. the chloride level. Results show that at temperatures between 40°C and 80°C, indium–activated anodes undergo operating potential ennoblement (electrochemical potential shifts in the electropositive direction), and there is consequently a reduction in current capacity. It is remarked that the corrosion morphology at ambient temperature had an "even distribution of pits over the anode surface and corrosion products were not adherent" whilst at temperatures over 70°C attack had a "more irregular surface morphology, with deeper and larger pits and grooves [7]. It is illustrated that the anode current capacity values in case of high temperature (80°C) seawater applications are in the range of 720-900 A.h/kg [4&5] respectively; however, the reported anode potential w.r.t Ag/AgCl seawater reference electrode is limited to -1,00v [4&5]. Furthermore, it has been concluded that the concentration of chloride has an impact on the free corrosion

potential of Al-based anodes. Additionally, the pitting potentials are influenced by changes in chloride and sulfate concentration, as well as the chloride/sulfate molar ratio [8]. A potential value -1,00v is reported as anode potential in case of anode is buried in seawater sediments, i.e. low chloride content with normal operating temperature (ambient). However, a significant reduction in current capacity is noted, which is limited to 1500 A.h/kg [4&5]. When low chloride and high temperature are combined, it is crucial to pay close attention because the anode current capacity is significantly reduced to a range of 680-800 A.h/kg [4&5] at an application temperature of 60°C. This represents only 27.2-32% of the reported typical current capacity of 2500 A.h/kg [23]. Nevertheless, if the application temperature is 80°C, the anode current capacity is lowered to a range of 320-400 A.h/kg [4&5]. This represents only 12.8-16% of the quoted typical current capacity of 2500 A.h/kg [23].

The effect of DEH on the Al anode performance should be given higher attention as a significant influence was illustrated for the corrosion behavior of sacrificial Al anodes under the application of AC. Corrosion of the anodes, resulting from the current provided for the protection of the steel and self-corrosion, occurred at an increasing rate with applied AC level. The experimental study [11] has demonstrated that steel does not receive adequate protection from sacrificial anodes when AC is applied. This demonstrates that there is a drop in the efficiency of the anode when AC current is present. Furthermore, the author [9] described the impacts of the DEH system on the performance of the Al anodes; this is evidence that the effects of the CP anodes on the DEH system and vice versa should be taken into consideration. The outcome was published by the author. To better understand the impacts of AC on the capacity of the Al anode, the author suggests doing additional tests in the future.

The tests [15&16] clearly demonstrated a marked difference between the use of Al and Zn anodes, in particular with respect to pH. For Al, after an initial ten weeks in which the pH hardly changed, a sudden reduction of the pH from pH 8 to pH less than 5 was noted. The Al hydrolysis is a main factor in reducing the pH, which is initially buffered by the bicarbonate within the seawater. On exhaustion of the bicarbonate, the pH is reduced, causing acidification of the seawater. Zn anodes did not replicate this fall in pH. Whilst the greater anode capacity of Al anodes makes them lighter and easier to install and less costly than Zn anodes, the latter is a more secure choice if there is no inadequate or uncertain replenishment of the electrolyte. It was concluded that despite significantly lower anode capacity for Zn-based sacrificial anodes, the total number of anodes to be installed could be reduced considerably compared to the use of Al anodes for a design life of more than 10 years. The chemistry changes in non-replenished, closed systems and consequences of reduction of the Al anode efficiency shall be considered in case of selection of Al anodes. These changes shall be addressed in internal structure CP designs. It was noted that the surface of the Al anode may undergo a change as a result of the formation of the passive oxide film during the conditions of cyclic immersion. Upon curing in the atmosphere, certain corrosion products that are produced during the immersion period may remain affixed to the surface and may be difficult to remove when the material is re-immersed in the subsequent cycle.

The activation of the anode is influenced by these factors, which increase the difficulty of oxide film breakdown and decrease the active surface area. Consequently, the anode exhibits a more positive operating potential and an open-circuit potential at a constant working current density following cyclic immersion. The adherence of corrosion products to the anode surface results in the formation of local macro-cells, which in turn leads to local corrosion and an irregular morphology of dissolution as the number of wet/dry cycles increases.

The capacity and current efficiency of the anode are significantly reduced by this local corrosion. If Al anode strikes a rusty surface, a thermite spark may be generated. Therefore, its use is restricted in tanks where there may be explosive atmospheres, and there is a risk of the anode falling. Al anodes are not recommended to be installed on the cargo / crude oil tanks, the tanks adjacent to cargo tanks / crude oil, or on any locations where the potential energy exceeds 28kg.m. It should be noted that the tank's integrity may be compromised by the improper placement of Al anodes. This can occur in the event of cyclic immersion conditions, which may result in a decrease in anode efficiency, or in the event of an anode dropping, which could generate a thermite spark. Consequently, it is imperative to advocate for a uniform and explicit policy regarding the installation of Al anodes. Although there is a lack of clear information regarding the effect of Al formation on humans and Al is not clearly recognized as a toxic metal; however, several studies have reported neurotoxic reactions on animals during laboratory experiments [19], and it also affects birds and mammals through the food chain indirectly.

In the aquatic environment, Al acts as a toxic agent on gill-breathing animals such as fish and invertebrates [20]. An important difference between the Al form in seawater and the Al form in freshwater is that there is no cation in the seawater, and it is very strong under acidic pH conditions. The author recommends further investigation regarding the toxicity impaction of Al formation in humans (it may be possible to establish this as there is a toxicity impact on animals and fishes). Based on the aforementioned discussion and the efficiency of the Al anode in the presence of a low chloride electrolyte (e.g., drinking water), as well as the likely deleterious toxicity impact of Al formation on humans. The author should clarify that the Al anode is not to be employed

in the event of CP protection of drinking water internals from the perspective of operation and safety restrictions. It has been clearly stated that Al alloys are only suitable for environments with salinity levels exceeding 5 g/kg (mass fraction 0.5%), which are typically found in brackish or seawater environments with resistivity below 2 Ω.m [23]. However, this is not the case in drinking water tanks.

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