SACRIFICIAL ANODES FOR CATHODIC PROTECTION IN SEA WATER: A REVIEW

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The application and performance of various anodes used in cathodic protection of offshore structures are discussed. Only galvanic type is considered. The relative costs of various anodes, together with the better performance indicate that aluminium alloy anodes will have a better future in the days to come.

Cathodic protection to mitigate corrosion is generally used in conjunction with protective coatings by establishing a sufficiently negative potential on a submerged structure, mainly ships, to make the entire structure cathodic. Cathodic protection can be obtained using either relatively inert anodes with an impressed voltage from an external power source or from sacrificial galvanic anodes such as zinc, magnesium or aluminium. Galvanic anodes depend on their inherent electrochemical activity for driving voltage and are a self-contained power source when coupled to a more noble cathodic metal. This paper is written with a view that it should serve as an overview on galvanic anodes (metals and alloys) that are available in literature for the sacrificial protection of ships.

Requirements of an anode material

Since a knowledge of the essential requirements of sacrificial anodes serves in better appreciation of the topic, the same are listed below.

1. The anodes must have a solution potential sufficiently negative to polarize a steel structure reasonably quickly to a potential more negative than -0.80 volt. However, the potential should not be excessively negative to cause wasteful and unnecessary passage of current to fully protected steel. The practical range of potentials is limited to about -0 95 to -1.6 volts.

2. The anode must not polarize to any great extent when delivering current, that is, it must not develop a passive film or obstructive corrosion products.

3. The material must have a high electrical output in ampere-hours per pound.

4. The anodes should corrode evenly and uniformly.

5. The material should be easily available and easily cast or formed into various shapes and sizes.

6. The material must be reasonably inexpensive so that, in conjunction with suitable electrochemical characteristics, protection can be achieved at a low cost per ampere-hour.

A critical look at the above requirements indicate that only zinc, magnesium and aluminium alloys can be considered as practicable sacrificial anode materials. The theoretical electrochemical properties of these materials are given in Table-I. The three anodes are individually dealt with below :

TABLE-I Theoretical Electrochemical Properties of Anode Materials

Metals	Potential Volts	Electrochemical equivalent	Output amp. hr/lb.
Zn	—1.05	0.339	372
Mg	—2.66	0.126	1000
Al	—1.96	0.093	1352

Zinc anodes

Sir Humprey Davy[1] endeavoured to control corrosion of copper sheathing on war ships by the current generated by the galvanic corrosion of zinc. From then on, the use of zinc as sacrificial anode was increasing. Zinc provides a 1.1 volt solution potential to a saturated Cu-$CuSO_4$ reference electrode in either sea water or gypsum–clay back fill[2]. Galvanic efficiency of 95% is obtained in sea water[3]. These high and dependable efficiencies favourably indicate the use of zinc anodes for sea water applications. These anodes possess two outstanding technical advantages:

1. The anodes are self regulating, which means that they can be fastened directly to the hull and therefore require no attention.

2. Excellent current distribution can be obtained by locating anodes close to the various high cathode demand areas on the ship. The electrochemical characteristics of zinc anodes are summarized in Table II.

Table-II Electrochemical and Physical Characteristics of Zinc Anodes

Theoretical ampere-hour per pound	372
Current efficicency, percent	95
Actual ampere-hour per pound	354
Solution potential, volts (anodic to saturated Cu-$CuSO_4$ reference)	1.1

Corrosion of Zinc

The current output of zinc anodes is restricted, after a short period of time, because of the formation of a dense adherent. resistive corrosion product on the metal. The corrosion of zinc is by a divalent reaction. The corrosion pattern of the anodes is very uniform.

Zinc alloy anodes

Several investigators working on zinc anodes came to the conclusion that the presence of iron in zinc anodes is detrimental to the performance and iron must be limited to 0.0015% maximum [4,5]. Addition of certain alloying elements such as aluminium or aluminium plus one other element resulted in more effective anode and the new alloying elements permit an increased iron content in zinc anode. Waldron and Peterson[6] showed that zinc anodes containing iron upto 0.006% and small additions of aluminium (0.5%) and cadmium (0.1%) gave higher total current outputs than high purity zinc anodes. Carson[7] proved that alloyed anodes (0.3% Al or 0.1% Al + 0.05% Cd) is reliable and are capable of providing complete cathodic protection for ship hulls for extended periods in sea water. These materials do not polarize with time. According to Crennell and Wheeler[8] the detrimental effect of iron in zinc anodes is overcome by the addition of Al (0.5 – 1%) and Silicon (0.25 – 0.5%). The iron is believed to be bound as a ferro-silicon compound and in that form to be unable to act in the damaging way that free iron does.

Latin and Cook[9] have shown that corrosion can be controlled with zinc anodes in tanks alternately carrying crude oil and sea water ballast. Amber[10] has concluded that zinc anode current output is normal during the ballast cycle in a vessel carrying mixed cargoes. He found that petroleum products and waxes did not accumulate in anode corrosion products during a two year service test.

The development of Hi-Amp (Trade name for zinc alloy anode) zinc alloy found wide use in all applications where magnesium was used. The Hi-amp has many advantages over magnesium anodes : (1) Lower cost per ampere hour of current delivered (2) no tendency toward incendive sparking (3) elimination of overprotection locally or otherwise (4) elimination of hydrogen accumulation hazard and (5) self regulating characteristics.

The main disadvantages of zinc anodes are :

(1) Considerably more anodes required to provide total protective current and (2) increased dead weight.

Magnesium anodes

Magnesium is used in much the same way as zinc as sacrificial anodes in cathodic protection. An important advantage of magnesium is the higher effective potential of that is developed[11]. Three electrochemical properties of magnesium suggest its usefulness as a sacrificial anode. (1) It possesses a high driving voltage to protect steel (2) It has a low electrochemical equivalent and (3) it has good anodic polarization properties. Its properties are summarized in Table-III.

Table-III Electrochemical and Physical Characteristics of Magnesium Anodes

Theoretical ampere-hour per pound	1000
Current efficiency percent	50
Actual ampere-hour per pound	500
Solution potential volts	–2.66

Magnesium is found to corrode by a univalent reaction. The metal is consumed uniformly.

Magesium ribbon anode

The economical importance of using magnesium ribbon anodes (for prepolarizing) in conjunction with the heavier permanent - type magnesium anodes has

been stressed years ago[12,13]. By prepolarizing the steel surfaces (50 mA/sq.ft.) with the short lived magnesium ribbon, the current density for maintaining protective potentials can be reduced to 3 mA/sq ft. The high initial current density stabilizes the current requirements with respect to time. This permits the use of a considerably smaller permanent anode installation with a savings in current of approximately 40%.

Magnesium jacketed zinc anode

This was first made commercially available in 1963 and has since had phenomenal use in the growing trend to offshore long-life galvanic anode systems[14]. This anode is actually a composite of two anodes, namely, zinc and magnesium. It may be pointed out that the magnesium-clad zinc anode is simply a compromise between the earlier prepolarization technique using magnesium ribbon and no prepolarization at all.

Magnesium alloy anodes

It is well known that commercial, pure magnesium possesses a high solution potential; however the current efficiency was not dependable. George et al[15] developed a new alloy anode containing manganese. The new alloy anode had the capability of tolerating higher iron contents without a detrimental effect on current efficiency. Manganese is believed to offer a means of combating the adverse effect of iron without actually removing it.

Robinson and George[16] have shown that the efficiency of magnesium alloy anodes can be adversely affected by certain impurities like copper, nickel, iron, lead and tin. Robinson[17] reports that high purity Mg-Al and Mg-Al-Zn alloys perform much more efficiently than pure commercial magnesium at current densities upto about 700 mA/sq.ft. Magnesium can be used to make a high driving voltage anode. It is universally applicable and is not affected by its environment.

Disadvantages

The metal is light and so has a high volume consumption and this coupled with a poor efficiency at low current densities means that the anode cannot be used economically to give long life. It is comparatively expensive metal and at present-day prices its cost per ampere year is about 50-60% higher than the other sacrificial anode materials.

Applications

Magnesium anodes have been used to prevent corrosion of galvanised and glass-coated steel hot water tanks so as to extend their life and avoid the so-called rust red water[18].

Aluminium anodes

The most common non-ferrous metal that should act as a sacrificial anode to steel is aluminium. Theoretically aluminium shows an adequate potential and because of its very high theoretical current output, possesses a two-fold cost advantage over the other two metals. However, the utility of pure aluminium has yet to be realized in a sacrificial anode because of a protective oxide surface film which limits its actual solution potential to 0.7 volt (vs. SCE) and its current capacity is only about 400 amp. hr/lb. The electrochemical characteristics of aluminium anodes are summarized in Table-IV.

Table IV Electrochemical and Physical Characteristics of Aluminium Anodes

Theoretical ampere hour per pound	...	1350
Current efficiency percent	...	95
Actual ampere-hour per pound	...	1295
Solution potential volts	..	– 1.1

It is well known that elimination of cathodic low hydrogen overvoltage impurities such as copper, nickel and iron increases current capacity by decreasing the number of local corrosion cells on the anode surface. Increasing the purity of unalloyed aluminium does increase its current capacity but alters the solution potential only slightly in the anodic direction. The solution potential of aluminium could as well be altered by alloying and this resulted in binary and ternary alloys with properties particularly suited to cathodic protection in sea water.

Aluminium alloy anodes

Many investigators[19,20] tried zinc as the alloying element and found that the potential of an Al-Zn alloy becomes progressively more anodic upto a zinc content of about 5% but increases only slightly with further additions of zinc. In sea water, anodes of this alloy have an average current capacity of 725 amp. hr/lb.

Exceptionally high potentials have been recorded by alloying with metals such as tin, bismuth, indium and gallium. Of these, the most promising are the aluminium-tin alloys[19] which exhibit a potential around-1.3 volts. However, aluminium simply alloyed with tin does not produce good anodes because it will rapidly polarize and both potential and current flow decline to low values. The initial potential and polarization characteristics were improved by suitable heat treatment.

Newport and Reading[21] considered the alloying effect of 37 elements and their combinations. Mainly to ternary alloys became popular and they are [1] Al-Zn-Sn and [2] Al-Zn-Hg. The former require critical and closely controlled heat treatment; otherwise unpredictable low current efficiencies will be observed in laboratory testing. On the other hand Al-Zn-Hg anodes required no heat treatment and the current efficiency was reported as 1300 amp. hrs/lb of metal expended over a current density range of 50-1500 mA/sq.ft.

The relations between alloy composition and anode performances of Al-In-Zn and Al-In-Zn-Cd alloy anodes under various exposure conditions were studied by Sakano et al[22]. In addition, the effect of heat treatment of anodes and some observations suggesting the mechanism of activation of aluminium by alloying are described.

Lennox et al[23] studied various aluminium alloy anodes and prefers an anode of the composition Zn-0.56%, Hg-0.04% Fe-0.06% balance Al since this alloy reflected exceptionally stable close circuit potential values with time, consistent current output characteristics with time, and the extremely high average current availability of 1300 amp. hrs/lb. Burgbacher[24] reports an efficiency of 95.8% for Al-Zn-Hg anode. He has also conducted field test studies on these anodes for 244 days.

Applications

Use of aluminium anodes could provide a considerable economic advantage if the high theoretical amp. hr/lb. capacity of aluminium was realized in practice. Also, use of light weight anodes as a substitute for zinc anodes is attractive for cathodic protection of weight-limited structures such as submarines and instrument packages used in the deep ocean. Aluminium anodes can also be used wherever protection with magnesium-type anode would be a problem.

Relative costs

The relative metal costs per ampere year for zinc, magnesium and aluminium anodes are summarized in Table-V. The relative cost/amp. year of Al-Zn-Hg anodes approximately two thirds that of zinc anodes and approximately one half that of magnesium anodes.

Table–V Relative anode cost/amp. year

Anode material	Relative cost based on actual ampere–hour per pound in dollars
Zinc	1.00
Magnesium	1.31
Aluminium–Zn–Hg	0.67
Al–Zn–In	0.77 to 0.93
Al–Zn–Zn	0.62 to 1.7

Table–VI Characteristics of Commercially Available Sacrificial Anodes in Sea Water Service

Anode	Description	Solution potential Volt	Current efficiency-%	Amp. hrs per pound	Remarks
Magnesium	0.03 Cu(max.) 0.003 Fe(max.) and 0.10 Mn(min.)	– 1.50(1)	50	500	
Zinc	99.99% pure	– 1.05(1) – 1.00(3)	95	354	
	99.9% pure Al	– 1.05(2)	95	1280	No heat treatments required
Al–Zn–Hg	0.045 Hg + 0.45 Zn	– 1.1 (3)			Good efficiency
Al–Zn–Sn	4.3%Zn + 0.13%Zn 0.07 Fe	– 1.1 (3)	85	1150	Requires precise control of heat treatment

1. Close circuit potential referred to Ag/AgCl electrode
2. Close circuit potential referred to saturated calomel electrode
3. Close circuit potential referred to Cu–$CuSo_4$ electrode.

Conclusion

The characteristics of commercially available sacrificial anodes in sea water service are shown in Table-VI. Aluminium alloy anodes are gaining popularity and it can be predicted that it will largely replace magnesium and zinc anodes for sea water applications. The cost evaluation of galvanic anodes shown in Table-V also indicate that aluminium alloys are the cheapest materials for cathodic protection compared with zinc and magnesium alloys.

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