Technical Section

RECENT DEVELOPMENTS IN THE APPLICATION OF CATHODIC PROTECTION TO MARINE CORROSION

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Abstract

The importance of cathodic protection as a preventive method either alone or in conjunction with other methods such as protective coating in the field fo marine corrosion has been outlined. Recent developments in the matter of choice of anode systems automation, and operating data, and some illustrative applications, are discussed. Besides, a few case histories have been cited, and the economics of the problem has been touched upon.

A. Introduction

The advent of cathodic protection (C. P.) has given a new dimension to the technology of combating corrosion. In the protection of marine structures and ships the method has found extensive application though paint is also widely used. The protective coatings, however, are not capable of discontinuing the corrosion process to the required degree. Perhaps C. P. is one anti-corrosion technique which when correctly applied can be guaranteed to give perfect protection. But it is always the economics of the problems that dictates the choice of the protection method. The present article reviews the recent developments in the application of C. P. to corrosion problems concerning the commonly encountered marine structures and vessels. The literature reference includes the Chemical Abstracts, the Corrosion Abstracts, some original articles, and proceedings reports published since 1967.

B. Theoretical Aspects

The fundamental mechanism of all corrosion is corrosion cell comprising an anode, a cathode, an electrolyte and a return path between the electrodes. The degree of activity of the cell depends upon the resistivity of the electrolyte and the voltage difference between the electrodes. The cell can exist in a dormant state to be triggered into action in the presence of a low resistance electrolyte. To combat corrosion either the cell must be stifled, or it must be mitigated to a degree compatible with the problem. A corrosion cell will cease to exist if one removes any or a combination of these parts. An elegant method of countering corrosion on this basis is C. P. The introduction, in the last twenty years, of new anode materials and instrumentation techniques has considerably widened the field of application of C. P. The theoretical aspects of the problem have been dealt with in many articles.

C. Instrumentation and Automation

The continuous nature of C P. in marine applications makes instrumentation and automation an absolute necessity. An automatic control claimed to be the best for the widest variety of applications is the Si-controlled rectifier or the thyristor[12]. A new C. P. system is also described[13] for marine appliances, which overcomes some of the disadvantages encountered in the conventional impressed-current system of one-step transformer rectifier type. It consists of a main control transformer (out put

60–200v) and several small transformer-rectifier sets (output 13-0-13v) installed at a short distance from the electrodes used for protecting the structure. In this system the power loss in the wiring circuits is negligibly small because of much shorter d. c. wiring than that of the conventional one-step transmitter rectifier type. Besides, the C. P. by two-steps transformer rectifier type is supposed to be more economical than the one-step transformer rectifier type.

For submerged metallic structures a C.P. apparatus is described in a patent[14]. A number of water-tight buoys each containing a rectifier and a transformer serves as a d. c. source. They are connected in various assemblies to give the desired current and voltage values. Yet another C.P. circuit[15] containing diodes, transformer amplifier, a sacrificial Mg anode and a Ag-AgCl reference cell, eliminate the need for external power sources and manual adjustments and provides for close control of the potential. A patent[16] describes a C. P. for the protection of cooling space of sea water-cooled diesel engines A thin film of H_2S is produced (from the electrolysis of sea water) on the surface to be protected. Chlorine developed is vented to the atmosphere without loss of coolant. For coping with fouling action in sea water a high purity Mg sea water battery is developed for long period of action[17]. An appliance is also described[18] which enables the slow deterioration of paint films in Sea-water to be followed by studying the changes in ohmic resistance of painted pieces.

Human failure in the application of C P. to power station cooling plants can also be overcome by automation. A practical equipment is detailed[19] using a fifty-channel commutator selection device, coupled with a digital voltmeter display to give either a 'direct' or an 'alarm' method of operation. Instruments and methods similar to those described above are also detailed in other articles[20-29].

D. Installation Design

Design plays an important part in a C. P. system. C. P. will be most effective if it is made to follow accepted engineering principles to reduce interference with other metallic substructures and to withstand mechanical hazards. Each case has, of course, got to be considered individually. In fact corrosion prevention should begin with initial design. For instance, in the case of shipboard protection a remote anode system can be installed on the ship's hull if proper consideration is given to anode geometry, voltage and area of anode shield[30]. Anode locations should be in areas where mechanical abrasion of paint is least likely to occur. Ship cathodic protective systems, in general, should be so designed as to locate anodes on areas of ship hulls with a minimum of locked-in space or anticipated external stresses[31].

The effectiveness of C. P. in condenser water boxes (using sea water) is again a matter of design. Test result showed that it was advantageous to set many of the anodes as near as possible to tube plates (within 600 mm.) especially in the case where galvanic anode system was adopted[32]. The C. P. of ship hulls has been achieved in an instance with the help of an anode consisting of a thin Al wire, 60 metre in length and trailing in the sea[33].

One of the design criteria for a good offshore pipeline under C.P. is an 18 in. minimum clearance from foreign lines[34]. For C. P. offshore platforms and pipeline, the design factors for maximum protection are described[35,36]. Design considerations for the C. P. system of regulator gates have also been described[37]. Few other design considerations have been reported[38-49].

E. Sacrificial Anode System

In this system of C. P. the protective current originates from galvanic anodes. The direction of current in a galvanic cell comprising dissimilar metals depends on the particular metal combination. For example, current will flow through sea water from steel to copper with consequent corrosion of steel, but on the other hand will flow from Mg to steel with corrosion taking place on the Mg surface.

In a sacrificial anode system a series of anodes usually of Mg or Zn are attached to the underwater portions of the vessel's hull and the electrolytic action in seawater is such that the anode is consumed before any corrosion takes place on the steel surface.

The size and current potentials of the anodes depend on the area to be protected and on the length of the anode life required by the ship owner. Consideration must also be given to the fact that the larger the anodes the more hull resistance is provided with consequent decrease in speed and increase of oil and fuel consumption. Economic factors, therefore play a decisive part in the extent to which the shipowner adopts systems of C. P. Here some new types of anodes are considered.

E. I. Zinc anodes:

It is reasonable to deduce that 85% of all applications of C. P. to hulls are achieved by use of galvanic anodes based on Zn or Al alloys. Pure zinc can provide C. P. to mild steel in sea water but serious corrosion may occur if the zinc anode is impure. Rapid corrosion of rudder (steel) on a fishing vessel in the port of Haifa, Israel, provided an example[50]. The wooden vessel had a protective sheet of copper covering its bottom. Blocks of low grade zinc were fastened to fight corrosion. Within one month after the vessel was launched the rudder and other metal parts were so badly corroded that the vessel had to be taken out.

The relatively low driving potential of pure zinc against steel has proved, in marine installations, to be far more of an advantage than a drawback because, the trend is toward long-life galvanic anode systems, for which zinc is naturally suited and Mg has little utility. Conversely zinc is ill-suited to short-life suspended anode systems where Mg is most widely used in marine work today.

Zinc ribbon anodes, recently introduced, are being accepted quite rapidly as a new development in the C. P. field*[51]. The principal advantages of ribbon sacrificial anodes are (1) high current output to volume ratio, (3) uniform current density applied to long cathodes and (3) low installation cost as related to the unit of current delivered to the structure to be protected. The electrochemical properties of zinc shown in table 1 indicate that it can be effectively used as a ribbon sacrificial anode.[51]

Table 1

Electrochemical properties of zinc

Current Capacity, amp/hrs/1b	372
Current efficiency, %	90
Actual current cap., amp/hrs/1b	354
Consumption, actual, 1b/amp year	24.8
Solution potl, Volts (sat. $Cu/CuSO_4$ elec)	1.1

Another method of application of zint as anode is to prepare an adhesive containing 5-60 % of homogenously distributed zinc powder (0.05-0.2 mm particle size) which can be glued tothe surface to be protected. The shear strength in 1000 Kg/cm^2 of coldhardened bonds with 10% zinc powder was 1.2. The bond was not affected by exposure for 3 months to sea water or fuel oil[5].

Zinc alloys as anodes:

The influence of various alloying elements like Cd,Mg, Al etc., on the behaviour of zinc anodes and also their effect with cathodes coated with various types of paints have been reported [53,54]. The present state of C. P. with zinc for marine structures in France, is to use zinc alloys of composition Zn + Fe0.004 + Al 0.1 + Cd 0.05%[55]. Many offshore oil drieling installations [55—57] and buoys [58] make use of zinc-rich coatings as anode for C.P. Zinc amalgam electrodes have also been used in certain cases [59]. Few other instances of the use of zinc and zinc base alloys for C P. have been described [4,28,60-63].

Case histories:

Though laboratory and field tests give good indications of a material's performance, sound data from actual installations cannot be surpassed. A few case histories are presented here des-

* Zinc ribbon referred to here is marketed under the trade name Diamond Line, by the American Smelting and Refining Co. Federated Metals Dicision, Broadway, New York.

cribing the performance of zinc anodes in actual use. (1) A mammoth suffolk representing an investment of $ 1,750,000, used for pumping sand, grit and gravel from the floor of Mt. Sinai harbour; off the north shore of Long Island, N. Y, owing to continuous operation has little dry-dock time. Proper maintenance is the vital part of her working efficiency. A specially engineered C. P. system using zinc anodes, protects the dredge from corrosion. [60].

(2) The Toms River chemical Co., New Jersey built a $ 2 7 million, 28 in. dia., and 10 miles long pipeline to discharge its treated effluent into the ocean. After a series of corrosion tests, sacrificial zinc ribbon anode was specified to suppliment a coal-tar coating[51].

(3) Internai protection of tankers:—When the U. S. Coast Guard prohibited the use of Mg and restricted the use of Al anode in tankers carrying volatile combustibles in U.S. flag ships, no limitations were imposed on the application of zinc [51]. This action in part has been responsible for accelerated use of zinc anodes in clean tankers[61].

E.2. **Magnesium anodes :**

Mg as an anode has had a substantial history of orderly development and use. Dow chemical company carried out extensive research on the adaptability of Mg an galvanic anode in marine appliances[66]. The higher driving potential (- 1.50 V open circuit to Ag/AgCl ref.) and lower density of Mg, means fewer anodes and much less weight than would be necessary with Zn for the same total protective current output, but the higher potential does in turn mitigate against long-life designs with Mg anodes.

Case history :—

In the C.P. of deep sea tanks the anode metal (in a finely divided form) is Mg, Zn or Al or an alloy of a mixture thereof[61]. A relative new comer to the field of galvanic anode is the Mg-jacketed Zn anode.[67]. It is a compromise between the earlier prepolarization technique using Mg ribbon and no prepolarization.

Economics of Mg-Clad zinc :—

The average cost comparisons in respect of 15 offshore platforms using Mg-Clad Zn anodes versus conventional Zn anodes showed a 15–20% saving[67]. The use of Mg as galvanic anode in marine C. P. has been described in a few other articles [68 69 33].

E.3. **Aluminium anodes :—**

In view of the light weight, low cost and high electro-chemical performance, Al should be the most attractive material for a long-life galvanic anode. With a possible output of 1352 amp. hr/lb corresponding to 6.4 lb/amp. year and at a cost of $0.48/lb. an Al anode would have to be only 50% efficient to equal zinc in economical value in the marine C.P. field[67]. In India Al as a prospective anode material has greater promise owing to the comparative abundance of this metal. Further the Al anodes now available have closed circuit potentials comparable to zinc (−1.00 V – 1.15 V with Ag/AgCl ref.)[67]. Consequently the driving potential is in the acceptable range and offers no hindrance to the economic possibilities of Al anodes as indicated above.

Aluminium alloys as anodes :

Additions to Al of metals like Ga, Sn, In, Bi, Zn, Cd Ba, and Be results in alloys with higher anodic potentials and higher anodic efficiency than the un-alloyed Al [70 71]. Certain combinations of these elements resulted in alloys superior to the single-element addition alloys. For example the alloy Al (99% pure) —0.045 Hg–0.45 Zn is found to be very useful as a sea water sacrificial anode. Field testing of 140 samples Al–Hg–Zn alloy anode conducted over 22 months in sea water showed that the alloy attains a potential of 1.05 V and gives an electrode output of 1280 amp./hrs lb. of Al consumed[73]. Thus the combination of high and reproducible efficiency, stable potential and stable current output gives the alloy significant value[72]. Another Al alloy for use as sacrificial anodes for the C.P. of ships has the composition Al (99.85%)-In 0.02-Zn 2.52-Cd 0.10%. It has a current efficiency of 83%[71]. Addition of Sn was also effective but produced anodes inferior to the In quaternary alloys[71]. Al metal powder in the form of fine coating on the hull surface of ship, also serves

as a useful anode material [73 87]. C.P. of marine structures with Al or its alloys other than that mentioned above has been described in many articles[74-86], [33 38 61 63 67].

A comparative cost evaluation of various anode materials to assist engineer is presented in a paper[81].

Case history :

A patent by the Shell International Co. describes the corrosion protection by C.P. with Al anodes in conjunction with a latex paint, of a large drilling platform submerged in the gulf of Mexico[88]. Field electrochemical efficiencies of the present day Al alloys range from 35 to 93%. However, excessive resistance between the anode metal and the cast-in steel brackets is a problem with Al anodes[89].

F. Impressed current system :

Cathodic protection with impressed direct current is an electrolytic process. The power supply is stepped down to low voltage d.c and the current is supplied to a small number of anodes attached to the marine structure and insulated from it. The anodes are usually platinized Ti[90-94 30 46 47] or lead alloys [95-98 41 93] and have a life of 10–20 years. Graphite also has been used in certain cases[99,100]. Platinized titanium anodes, besides remaining uncorroded can withstand erosion[46]. Also very thin Pt behaves like solid Pt, being extremely resistant to the action of O_2 and Cl_2 released by the anodic current. A further advantage is that such anodes can operate at high current densities[46]. Data are presented[30] to show that in the C. P. of ship hulls both Pb–Pt and Pt–Ti alloys can be used successfully. A lead based alloy containing 10–15 % Si has also been successfully used in C.P. of ship hulls. It is claimed that this composite anode surface has a passivity substantially equal to that of platinum[95]. It is interesting to note that the impressed current protection of Steel using Pt anodes greatly reduced corrosion in sea water but not in NaCl solution; presence of Ca or Mg ions was found to be vital[101]. Requirements for an ideal anode capable of being used over a wide range of impressed cd. are also summarized[46].

Costs and economics of the galvanic and impressed currrent systems:

A galvanic anode system costs approximately 4 cts/sq. ft/an. The intial cost of an impressed current system may be 5 times greater than a 2-year galvanic sys em but the former may last 10 years without replacement and power costs are minor. The life of the anode-shields is a critical factor in the 10-year cost comparisons between the two systems. A comparative study of the galvanic and impressed current anodes for protecting offshore structures is presented in a paper[67]. Specific examples relating to the economics of corrosion has also been detailed[102].

G. Operating Data.

In order that a C. P. system is effective it is necessary to maintain the optimal working conditions such as the potential, c.d., temperature and the geometry of the anode. The results obtained in the study of the influence of these factors are of practical importance. The application of lead alloy anodes for C. P. was studied from the corrosion loss in sea water of eleven Pb–Ag alloys containing concentrations of 0.41–4.91 % Ag, at pH 8.2 and at different temperatures[98]. The ideal alloying range has been found to be 2.0–4.5% and is independent of temperature. Similarly the effect of temperature and agitation on the formation of Ca–Mg deposits in cathodically protected steels in sea water have been studied[103]. In another instance the importance of the measurement of the potential in cathodic corrosion protection in sea water has been stressed[104]. The corrosion of sheet steel piling in twenty Danish harbours has been evaluated from underwater ultrasonic method[105]. Results of similar investigations have also been reported [106–115 72 73 78 84 86 90 92 98].

H. Applications

Here a few illustrative instances of application of C.P. to the marine structures and vessels are presented by way of case histories along with general considerations and the economics of the problem.

Shiphulls:

Corrosion prevention of ship hulls is in general achieved by the combination of coatings and C.P[116]. While a protective coating reduces the magnitude of C.E., if fouling were of no concern then it would be more economical

to protect the system solely by C.P. methods. The obvious saving with C. P. is that hull placement is practically never required. A further advantage is that the hull remains at its original smoothness rather than becoming progressively rougher over the years. The consequent saving in the fuel cost is considerable.

Treaters and tanks:

Corrosion damage to treaters and other oil field brine vessels in the past was considered an inevitable cost of producing oil. But with the present day equipment, materials and techniques available to the corrosion engineer, this waste need no longer be endured. Although a cent per cent protection is not possible yet, through C. P. the useful lives of these vessels can be economically extended. The economic and design factors of cathodically protected tanks, treaters and other vessels have been recently reported [117]. The average cost of uncontrolled corrosion in a treater was estimated to be $ 457/yr. while the average cost of C. P. is $ 137/yr.

Ballast tanks in general are protected from corrosion using galvanic Zn, Al or Mg anodes [18]. For petroleum cargo, only zinc is recommended since there is the possibility of flint action spark in the case of Mg or Al anodes. In such vessels C.P. is, however, better suited than coating.

Buoys:

In the case of buoys galvanic anode C.P. is widely in use[68]. As a certain amount of fouling can be tolerated in buoys, corrosion protection can be achieved solely by C. P. system. (without anti-fouling paints) using extra anodes. The approximate cost of protection is 3 ct/sq.ft/an.

Submarine pipelines:

Submarine pipelines are usually protected from corrosion both by coating and by C.P. Coating in general are not long lasting. The role of C.P. under these circumstances in to protect miscellaneous areas where the coating is or becomes imperfect inspite of precaution. The current requirement is usually small. Improvements in C.P. techniques bring special benefits to companies operating lengthy underground pipelines and marine terminals with extensive under water piping [119 120].

Wharves and similar structures:

Coatinng is impractical with warf piling since even the best coating does not last longer than 5 years. The economic and other advantages of cathodically protected uncoated steel piles are compared to coated steel piles, uncoated thicker piles, concrete and timber piles immersed in the sea at Lae in New Guinea[2].

Galvanic anode C. P. is normally used in the case of small wharves or where no power is available. It may also be used in dolphins which may be remote from a large wharf to which impressed current C. P. system is fitted. The anodes are normally suspended in large numbers amongst the piles and because of the wide distribution of anodes the potentials are usually quite uniform. A galvanic anode system requires practically no maintenance save annual inspection and potential measurement. The life of the anodes ranges upto ten years[2]. In large wharves and where power is no problem, impressed current C.P. is normally in vogue on account of its considerable economic advantage over the galvanic C. P. system. Also, protective currents of over 1000 amps. are common for large wharves and this would hardly be practical with galvanic anode system. The anodes may be fixed on brackets several feet away from selected piles and suspended beneath the superstructure or laid on the sea bed. In the case of land backed sheet piling wharves, anodes are located on both the land and water sides of the piling.

For water front structures such as quay walls and piers using steel piling mooring buoys and pantoon floats which are made of recently introduced special low alloy steels, corrosion protection can best be effected by C.P. Thus impressed current systems have been used to protect steel sheet piling and sacrificial Zn anode systems are used to protect fleet moorings[58].

France's tidal power plant:

Corrosion control investigations were made on the world's first hydroelectric plant to harness energy with an investment of $80 million on the coast of France. A complex system of anodes

comprising a wide range of interconnected metals was tested and the accomplishment of a satisfactory corrosion protection is rated as an achievement[121].

I. Conclusion

The above discussion indicates that cathodic protection provides the marine corrosion engineer and technologist with an important and effective method for the prevention of corrosion in marine structures and vessels. It will no doubt afford greater opportunities for future application owing to the challenge posed by new anodic materials and newer automation devices coupled with computors. In India, in particular with a greater availability of aluminium at a cheap cost (for use as anode) and with the availability of more abundant and chaper electrical power, cathodic protection technique system for protection of marine structures and vessels will no doubt attract greater attention in the years to come.

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