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# CADMIUM FREE GALVANIC ZINC ANODES

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**Abstract:** Galvanic anodes made of zinc alloys are commonly used in the fishing and marine industries for the protection of carbon steel and aluminum vessels, pipes, pumps and fittings, the most common being MIL-A-18001-K (ASTM B418 type I, which contains between 0.025 and 0.070 % cadmium and 0.1 to 0.5 % aluminum as alloying agents). In recent years, concern for the care of the oceans has led to actions that limit the use of certain metals in the manufacture of galvanic anodes (such as mercury and lead). Cadmium has been detected as a heavy metal highly contaminating marine life, which can be absorbed by plants and enter the food chain. The objective of this work is to manufacture cadmium-free zinc anodes for the fishing and naval industry with electrochemical properties similar to those obtained with zinc-aluminum-cadmium alloy anodes, capable of protecting carbon steel and aluminum in seawater.
**Keywords:** Zinc anodes, Cadmium, Electrochemical properties, Fishing industry.

## INTRODUCTION

Galvanic anodes are used for the protection of metallic structures in water or soil; in the sea, aluminum, magnesium and zinc alloys are used for the protection of vessels, port facilities, pipelines, pumps and accessories [1]. Zinc galvanic anodes are widely accepted for the protection of carbon steel and aluminum vessels due to their excellent electrochemical properties such as current capacity, current efficiency and closed circuit potential [2].

Zinc alloy MIL-A-18001-K (ASTM B418 Type I) contains cadmium and aluminum as alloying agents. Cadmium is a heavy metal that is classified as a contaminant of marine life [3] and poses a risk to human health as it is absorbed by plants and animals that feed on them. Cadmium is used as an alloying agent in the manufacture of zinc anodes to promote their dissolution in seawater and allow more uniform consumption.

For years the use of mercury in the alloying of galvanic aluminum anodes was fundamental, due to the properties obtained from this alloy (high current capacity and efficiency). Mercury had a determining role in the dissolution of aluminum anodes [4], however, at the beginning of the 21st century its use was banned because it is highly polluting to marine life and is potentially dangerous to humans if it enters the food chain [5]. Cadmium also represents a high risk of contamination of the oceans, which is why it is necessary to replace it [6].

Given this scenario, our objective is to develop a zinc alloy for cadmium-free galvanic anodes without detriment to their electrochemical properties according to the test method NACE-TM0190 "Impressed Current Laboratory Testing of Aluminum and Zinc Alloy Anodes", for this we will test other alloys such as aluminum and indium which do not represent a danger to marine life.

## EXPERIMENTAL CONDITIONS

### PROCESSING OF ZINC ANODE ALLOYS

The alloys were prepared in the foundry area of APC PROCESADORA ANAHUAC, S.A. de CV. Pure zinc alloys (ASTM B418 type II), zinc-aluminum-cadmium (Zn-Al-Cd, MIL-A-18001-K or ASTM B418 type I, this is our reference), zinc-aluminum (Zn-Al), zinc-indium (Zn-In), zinc-aluminum-indium (Zn-Al-In) were obtained.

### CHEMICAL COMPOSITION OF ZINC ALLOYS

The chemical composition of each alloy was determined by spark emission spectroscopy using a Bruker Q4 Tasman spectrometer.


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| Element | Pure Zn, %, pure Zn, %, %, %, %, %, %, %, %, %. | Zn-Al-Cd, %, % Zn-Al-Cd, %, %, Zn-Al-Cd, %, Zn-Al-Cd | Zn-Al, % Zn-Al, %, %, Zn-Al, %, %, Zn-Al, % | Zn-In, %, %, Zn-In, %, %, Zn-In, %, Zn-In, % | Zn-Al-In, %, %, Zn-Al-In, %, %, Zn-Al-In, %, Zn-Al-In |
|---|---|---|---|---|---|
| Zn | 99.99 | 99.78 | 99.47 | 99.95 | 99.44 |
| Si | <0.0022 | <0.0020 | <0.0020 | <0.0020 | <0.0020 |
| In | 0.0052 | 0.0043 | 0.0043 | 0.034 | 0.043 |
| Cu | 0.0007 | 0.0017 | 0.0006 | 0.0005 | 0.0011 |
| Sn | 0.0012 | 0.0017 | 0.0021 | 0.0029 | 0.0037 |
| Fe | <0.0010 | <0.0010 | <0.0010 | 0.0025 | <0.0010 |
| Cd | 0.0003 | 0.0560 | 0.0019 | 0.0009 | 0.0001 |
| Al | <0.0010 | 0.1600 | 0.5220 | <0.0010 | 0.504 |
| Pb | <0.0010 | <0.0010 | <0.0010 | <0.0010 | <0.0010 |

Table I. Chemical composition of alloys for zinc galvanic anodes by spark emission spectroscopy.

## PROTECTIVE POTENTIAL TESTS

Two cells for protective potential tests were fabricated in A-36 carbon steel and 5052 aluminum and galvanic anodes according to the alloys in Table I.

### PROTECTIVE POTENTIAL TEST CELLS

The cells were fabricated in 3 mm thick A-36 carbon steel and 3 mm thick 5052 aluminum, with dimensions of 203 mm in length by 150 mm in height and 90 mm in width. A protection current density of 80 $mA/m^2$ and an average anode life of 5 years were considered for the calculation of the required anode mass [7].

### Test anodes

The alloys described in Table I were gravity cast in carbon steel molds to obtain 400 g zinc anodes with carbon steel core and aluminum core for potential testing in carbon steel and 5052 aluminum tanks.

### POTENTIAL TESTS

The potential tests were carried out in accordance with NACE-SP0169 "*Control of External Corrosion on Underground or Submerged Metallic Piping Systems*" [8], placing the zinc anode with a core of the same material as the cell in synthetic seawater prepared according to ASTM D-1141 [9]. Potential measurements were carried out using a saturated Ag/AgCl reference electrode for 14 days.

## ELECTROCHEMICAL PROPERTIES

The electrochemical properties of each galvanic zinc anode defined in Table I were determined by applying the NACE-TM0190 test method at a controlled temperature of 23 $^{o}C$.

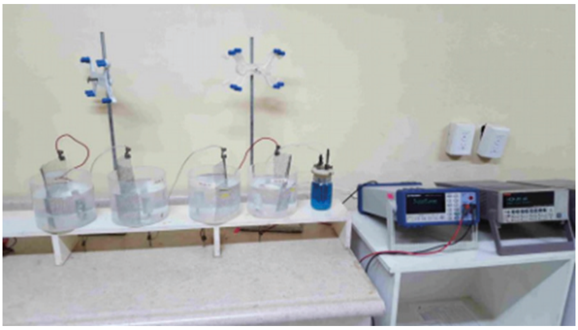

Figure 1. Development of the NACE TM-0190 tests.

## RESULTS AND DISCUSSION

Figure 2 shows the test results of galvanic zinc anodes with carbon steel core on carbon steel tank with synthetic seawater ASTM D-1141.

In the previous figure it can be observed that to protect the carbon steel tank in synthetic seawater the four alloys studied offer a protection potential lower than -0.800 V vs AgCl, which satisfies the NACE-SP0169 standard and higher than -1.05 V vs Ag/AgCl preventing overprotection of the structure.

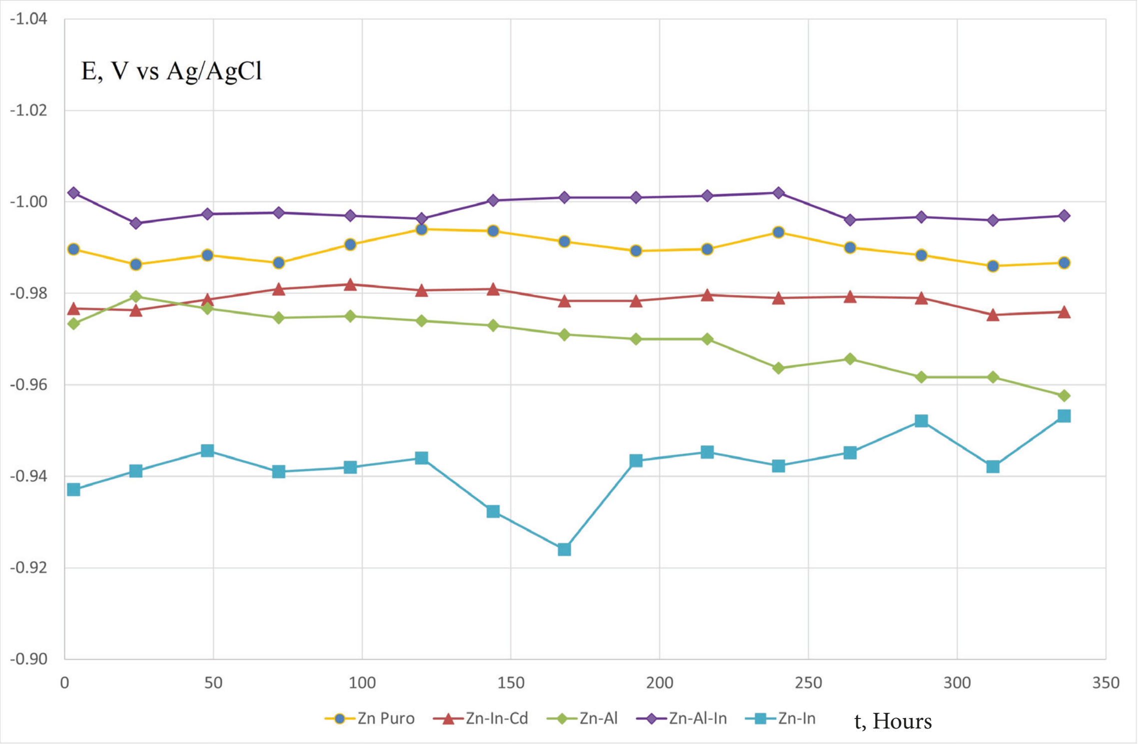


Figure 2. Protection potential of the carbon steel tank with seawater. ASTM-D1141 operating with different zinc anodes.

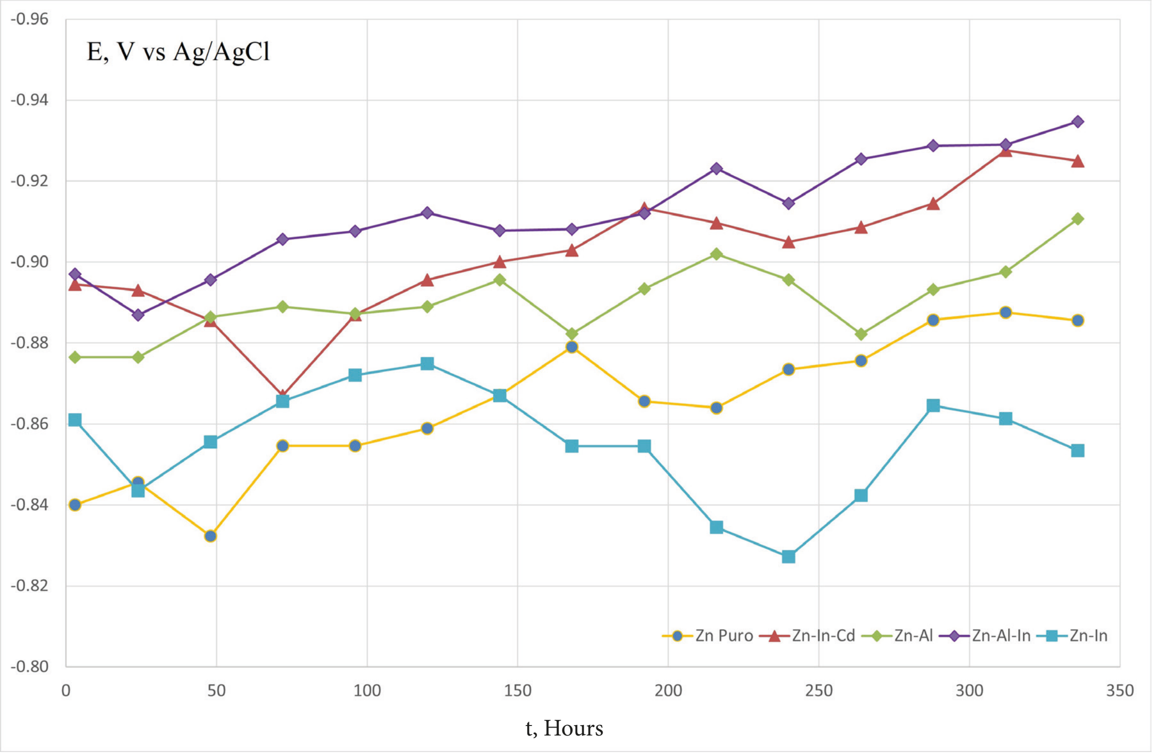


Figure 3. Protection potential of the 5056 aluminum tank with seawater. ASTM-D1141 operating with different zinc anodes.

Figure 3 shows the test results of galvanic zinc anodes with aluminum core on aluminum tank with synthetic seawater ASTM D-1141.

For the protection of the 5052 aluminum tank the Al-Zn-In alloy showed the best performance with potentials between -0.92 V and -1.0 V vs Ag/AgCl. If we consider that according to the NACE-SP0169 standard for aluminum alloys cathodic protection is achieved by obtaining a cathodic polarization change of at least 100 mV, this has been achieved since the potential of the 5052 aluminum tank without anode is -0.756 V vs Ag/AgCl.

The results of the determination of electrochemical properties according to the NACE TM0190 test method are presented in Table II.

| Alloy | Current capacity, AH/kg | Current efficiency, %, %, %, %, %, %, %, %, %, %, %, %, %. | Closed loop potential, V vs Ag/AgCl |
|---|---|---|---|
| Pure Zn | 791 | 93.9 | -1.000 |
| Zn-Al-Cd | 847 | 94.6 | -1.050 |
| Zn-Al | 762 | 90.8 | -0.990 |
| Zn-In | 807 | 96.8 | -1.009 |
| Zn-Al-In | 822 | 95.0 | -1.040 |

Table II. Electrochemical properties according to the test method. NACE TM0190.

The electrochemical properties obtained by the NACE-TM0190 method are similar for Zn-Al-Cd and Zn-Al-In alloys.

## CONCLUSIONS

This work has presented the evaluation of pure Zn, Zn-Al, Zn-In and Zn-Al-In alloys compared against Zn-Al-Cd alloy (MIL-A--18001-K, ASTM B418 Type I) in the protection of carbon steel A-36 and aluminum 5052 in synthetic seawater ASTM D-1141. In the protection potential tests the "cadmium-free" Zn-Al-In alloy recorded the best potentials for the protection of carbon steel (around -1-0 V vs Ag/AgCl) and aluminum 5052 (between -0.92 V and -1.0 V vs Ag/AgCl) complying with the NACE-SP0169 standards, while in the electrochemical properties it showed similar results to those offered by the Zn-Al-Cd alloy. Under this scenario, the "cadmium-free" Al-Zn-In alloy presents electrochemical properties similar to the MIL-A-18001-K alloy (ASTM B418 type I) and its performance for the protection of shipbuilding materials such as carbon steel A-36 and aluminum 5052 is acceptable, reducing the discharge of cadmium into the oceans. This alloy is an alternative to the use of Al-Zn-Cd for the protection of small boats, fish and shrimp farms.

## ACKNOWLEDGMENTS

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