v. 3, n. 29, 2023

Journal of
Engineering
Research

EFFECT OF INDIUM ON THE ELECTROCHEMICAL PROPERTIES OF ALUMINUM ANODES FOR THE PROTECTION OF CARBON STEEL

Ignacio García
Universidad de Guadalajara
Centro Universitario del Norte
Colotlán Jalisco

Ana Rosa Carrillo Ávila
Universidad de Guadalajara
Centro Universitario del Norte
Colotlán Jalisco

María Olga Concha Guzmán
Universidad de Guadalajara
Centro Universitario del Norte
Colotlán Jalisco

Leticia Lemus Cárdenas
Universidad de Guadalajara
Centro Universitario del Norte
Colotlán Jalisco

Abstract: Sacrificial anodes are made of alloys that are more electrochemically active than the materials they are to protect. For the protection of carbon steel, aluminum (Al), magnesium (Mg) and zinc (Zn) alloys are used. Aluminum alloys are widely accepted because they provide protection in different types of water (fresh, brackish and sea) and their low mass. In the "offshore" industry and in the protection of port facilities, aluminum alloy anodes ISO-15589-Part 2 *"Petroleum petrochemical and natural gas industries -Cathodic protection of pipeline trasportation systems-* Part 2: Offshore pipelines", have advantages over other types of alloys. In the cathodic protection of hot water tanks of domestic water heaters, this type of alloys have already begun to be used. In this work we explore the effect that indium has as aluminum alloy on its electrochemical properties according to the NACE-TM0190-2017 test method. "*Impressed Current Laboratory Testing for Aluminium and Zinc Alloy Anodes*".

INTRODUCTION

Since the late 1970s, the international scientific community and sacrificial anode manufacturers found it necessary to establish a test method to determine their electrochemical properties. The NACE (National Association of Corrosion Engineers) working group T-7L-2 and the ASTM (*American Society for Testing and Materials*) G01-09-02 T1 were in charge of this task, and by 1977-1978 they established the method test (NACE, 1978).

In 1989 tests were carried out with anodes based on the aluminum-zinc-indium alloy (Al-Zn-In) in waters of the Florida Keys (Lucas et al., 1989), some of them still contained mercury (Mg), which is currently prohibited due to its harmful effects on marine flora and fauna. In their conclusions, they highlight that the alloys containing Hg have a high current capacity (>2900 AH/kg), while the alloys with indium caused premature failures in the anodes.

Britton presented at the NACE Annual Conference a study on the results of the determination of electrochemical properties using the NACE-TM0190-90 test method "*Impressed Current Laboratory Testing for Aluminium and Zinc Alloy Anodes*". He concludes that the only source of error that can be attributed to the method is that the reference electrode is not calibrated (Britton, 1993).

The importance of aluminum alloys in the performance of a sacrificial anode is crucial, since we cannot use pure aluminum in the first place due to its ease of passivation. Zinc and indium have been gaining ground as the alloys par excellence for aluminum anodes, since they provide good activation. Second, the chemical composition and electrochemical properties are crucial for good anode performance.

The behavior of Al-Zn-In alloys for the protection of carbon steel in seawater has been studied, concluding that indium is the fundamental element to activate aluminum and prevent its passivation (Zoazua et al., 2008).

In drinking water, studies on the behavior of the Al-Zn-In alloy are few. At the end of the 80's, tests were carried out on drinking water with conductivities between 50 and 1500 S/cm. The results were not favorable for this alloy (Sheets *et al.*, 1989).

EXPERIMENTATION

CHEMICAL CHARACTERIZATION

PREPARATION OF THE ALLOYS

The alloys were prepared in a natural gas furnace and a 50 L capacity crucible, melting the aluminum up to 750 ºC and later adding the necessary amounts of zinc and indium to obtain the desired composition.

SAMPLE PREPARATION

The samples were prepared in accordance with the provisions of the NACE-TM0190-2017 test method, which establishes that they must be cubed with a length per side of 1 in (2.54 cm), that is, with a volume of 1in^3 (16.39 cm^3). The faces of each sample were machined by means of a bench mill.

DETERMINATION OF CHEMICAL COMPOSITION

The chemical composition of each sample was obtained by means of a Bruker model Q4 Tasman spark emission spectrometer, according to the ASTM E-1251 test method. "*Analysis of Aluminum and Aluminum Alloys by Spark Atomic Emission Spectrometry*".

ELECTROCHEMICAL CHARACTERIZATION

NACE-TM0190 TEST SET PREPARATION

The test kit (Figure 1) was prepared in accordance with the NACE-TM0190-2017 test method. A BK Precision model 5491B power source and a Keithley model 6220 multimeter were used. The applied current was 24 mA for 14 days, to provide a current density of 6 mA/in^2 (6.2 A/m^2). The charge that flowed through the circuit was confirmed by means of a coulometer made up of a pair of anodes made up of two high purity (>99.9%) copper plates, a 127 mm long 12 gauge copper wire as cathode, all immersed in a saturated solution of copper sulfate II (CuSO4). The mass of the copper wire was previously determined.

The test cell consisted of a cylindrical polycarbonate container with a 1 L capacity. A 13 mm circle was drilled in the bottom to insert a titanium rod that functioned as anode support and electrical connection. The cathode was constructed from ungalvanized carbon steel wire mesh. Synthetic seawater was used as electrolyte according to the ASTM D1141-(98)2021 method. *"Standard Practice for Preparation of Subtitute Ocean Water". The connections can be seen in figure 2.*

Prior to starting each test, the mass of each anode sample and each copper wire for the coulumbimeter was determined. The direct current of 24 mA was maintained during the 14 days of testing. The potential of each anode was obtained by means of a silver/saturated silver chloride (Ag/AgCl) reference electrode with a Lugging extension tube, at 3, 24, 48, 72, and 336 hours of operation.

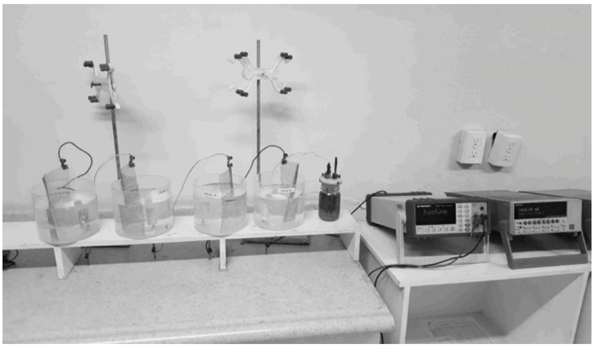

Figure 1. Equipment used to determine electrochemical properties according to the NACE-TM0190-2017 test method.

CALCULATION OF ELECTROCHEMICAL PROPERTIES

To calculate the current capacity, the mass of the anode (loses mass) and the mass of the copper wire of the coulometer (gained mass) at the end of the 14 days of testing were used.

$$\text{Current capacity (Ampere* hour/kilogram)} = \frac{C}{W} x1000 \quad (1)$$

Where C is the total current through the system in the 14 days (336 hours) and is calculated from the mass gain of the copper wire in the coulummeter (WCu) as follows.

$$C = 0.8433 W_{Cu} \quad (2)$$

Journal of Engineering Research ISSN 2764-1317 DOI 10.22533/at.ed.3173292324084

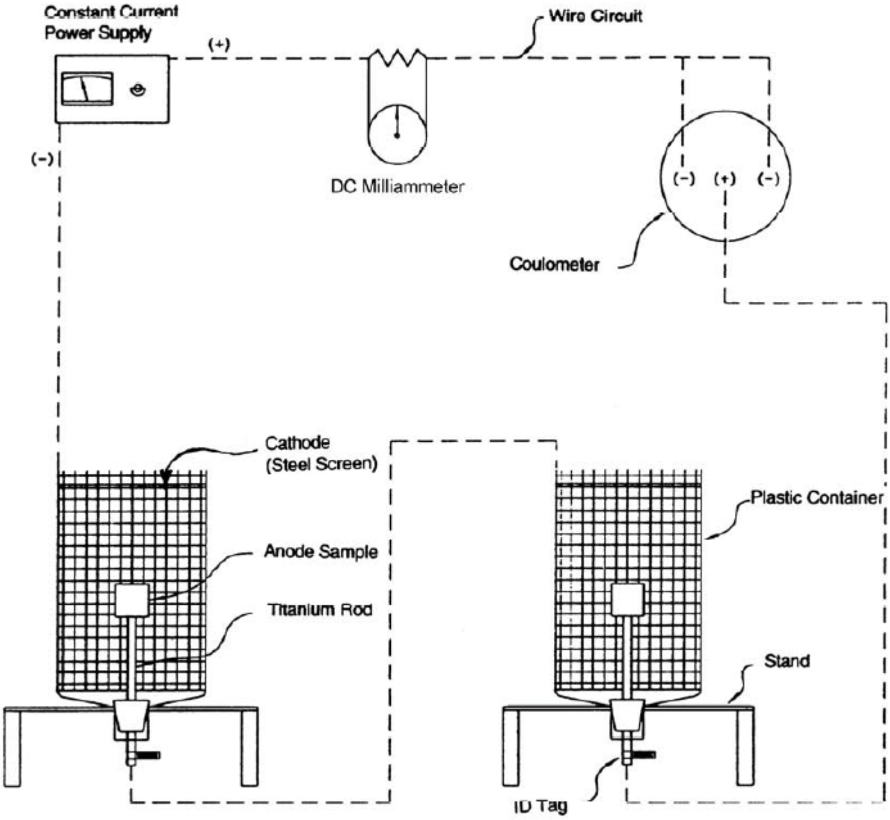

Figure 2. Equipment connection diagram for electrochemical determinations

Source: NACE-TM0190.2017

Sample/#	Conductivity / mS/cm	Potential/V vs. Ag/AgCl
1	100	-0.760
1	500	-0.810
1	50000	-0.925
2	100	-0.755
2	500	-0.815
2	50000	-0.910
3	100	-0.760
3	500	-0.822
3	50000	-0.890
4	100	-0.810
4	500	-0.880
4	50000	-1.150
5	100	-0.875
5	500	-0.900
5	50000	-1.198
6	100	-0.880
6	500	-0.910
6	50000	-1.230

Table III. Protection potential of anode samples Al-Zn-In at 25ºC.

The anode efficiency was calculated from the generation of hydrogen gas on the sample surface according to the following equation.

$$\text{Anode efficiency}\ (\%) = \frac{I \times 100}{I + \frac{132\,V}{t}} \quad (3)$$

Where I is the applied current (24 mA), V is the volume of hydrogen in milliliters (mL) obtained in the buret, and t is the time in minutes that the gas collection takes.

CATHODIC PROTECTION

To determine the protection that each alloy provides to carbon steel in different electrolytic media, a domestic L.P. gas water heater was used. of 40 L from a national supplier, testing synthetic drinking water with conductivity of 100 and 500 mS/cm, the type of anode used was a 6 "long x $^3/_4$" diameter pencil. The samples used were 4, 5 and 6. While for samples 1, 2 and 3 synthetic seawater (50,000 mS/cm) was used for the protection of a 20 L (15 cm) carbon steel tank. x 20 cm x 67 cm) of capacity, the type of anode was a 3 kg bar (20 cm x 5.6 cm x 3.7 cm). To determine the level of cathodic polarization of the structure, its potential was determined against a silver/saturated silver chloride (Ag/AgCl) electrode and the result was compared against that established in the standard practice NACE-SP0169-2013. *"Control of External Corrosion on Underground or Submerged Metallic Piping Systems"*.

RESULTS

Table I shows the alloys selected for this study, they were chosen from a total of 158 samples, seeking to be representative of six base alloys.

Sample/#	Aluminium/%	Zinc/%	Indian/%
1	97.47	2.50	0.016
2	97.45	2.48	0.020
3	97.44	2.51	0.025
4	97.38	2.50	0.030
5	97.38	2.49	0.035
6	97.36	2.50	0.040

Table I. Chemical composition of the obtained Al-Zn-In alloys by means of spark emission spectrometry.

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

Sample/#	Current capacity /AH/kg	Efficiency/%	Potential/V vs Ag /AgCl
1	2550	91	-1.030
2	2510	85	-1.051
3	2439	79	-1.055
4	2312	76	-1.070
5	2198	73	-1.085
6	2115	69	-1.100

Table II. Electrochemical properties of the obtained Al-Zn-In alloys through the NACE. TM0190 method.

Table III shows the protection potential of the 40L domestic gas water heater and the 20L carbon steel tank.

CONCLUSIONS

For protection in fresh water, the Al-Zn-In anode with an indium concentration from 0.030 to 0.040% works adequately, samples 4, 5 and 6 adequately polarize the structure of the drinking water heater hot water tank with conductivities between 100 and 500 mS/cm, generating potentials lower than -0.800 V vs Ag/AgCl. In seawater, anodes 1, 2 and 3 adequately protect by polarizing the tank structure at values more negative than -0.800 V vs. Ag/AgCl. Therefore, the aluminum anode alloyed with 2.5% zinc and with different concentrations of indium can be used for the protection of carbon steel in drinking water and seawater, which makes it useful to protect from the hull of a ship, port facility, offshore, even a domestic water heater.

REFERENCES

BRITTON, J. *Quality Assurance of Aluminum Sacrificial Anodes for Offshore Applications- A Practical Approach*, **Corrosion/93**, Paper No. 521, USA, 1993.

BROWN Jr., J.F. *Quality Control Testing of Aluminum Anodes: T-7L-2 Task Group Progress Report*, **Corrosion/84**, Paper No. 346, USA, 1984.

LUCAS, K.E.; PETRESON M.H.; GUANTI, R.J. *Long Term Performance of Aluminum Anodes in Seawater*, **Corrosion/89**, Paper No. 277, USA, 1989.

D.C SHEETS, D.C.; BROWN Jr. J.F. *Investigation into Cathodic Protection Design for Water Heaters*, **Corrosion/89**, Paper No. 287, USA (1989).

ZAZOUA, A.; AZZOUZ, N. *An Investigation on the Use of Indium to Increase Dissolution of AlZn Anodes in Sea Water*, **Materials and Design**, 29 (2008), p. 806, USA, 2008.