

Beneficial effects of electrolytic pastes and increased anode surface area on galvanic anodes instead of traditional backfill in soil applications.

Roberto Giorgini

Abstract

Concerning galvanic sacrificial anodes various factors such as anode current density, anodic reaction, anolyte composition, and alloy composition, can affect anode efficiency. For that reason anodes for industrial use are usually packaged in bags prefilled with suitable backfill material to mainly lower anode-to-earth resistance, increase current output and reduce self-corrosion, thereby improving efficiency. However, it has happened on several occasions that backfill material used failed as it had dried quickly and shrunk away from the anode reducing the current output and the efficiency of the anode.

The aim of this work is to evaluate the results of an experiment performed over a period of 6 months of a newly developed electrolytic paste for zinc sacrificial anodes in a simple simulated test procedure with the goal to overcome these backfill drawbacks. A total of three samples were prepared of which one sample was a traditional magnesium sacrificial anode with bentonite based backfill. The other two samples were zinc sacrificial anodes coated with the newly developed electrolytic paste of which one had an increased anode surface area by using a zinc mesh nonetheless with the same anode dimensions as the other samples.

During this experimental period current outputs and anode resistances were measured, evaluated and compared with the results of the traditional magnesium backfilled sample.

Introduction

Galvanic anodes have been used for decades to inhibit corrosion of steel structures.

The latest development to improve galvanic anode performance is the use of backfill material which is able to establish a more stable current output during the anode's surface life.

One of the main challenges when developing or designing backfill material for sacrificial anodes is to understand the electrochemical interactions between anode and backfill affecting the anodic reactions and the effects of surface area ratio between anode and structure.

This paper evaluates the results of a lab comparison experiment performed of a newly developed electrolytic paste for zinc sacrificial anodes over a period of six months. A total of three samples were prepared of which one sample was a traditional magnesium sacrificial anode with bentonite based backfill. The other two samples were zinc sacrificial anodes coated with the paste of which one of had an increased anode surface area by using a zinc mesh without changing the anode's geometry.

Experimental procedures

An experiment was conducted in which :

- Three sacrificial anodes were prepared with an equal geometrical surface area of 330 cm^2 . The magnesium anode was a commercially available anode with the dimensions (w/o backfill) of 2,74cm (dia) x 30cm (length) with a standard commercial backfill according ASTM G97-97(2007). The two zinc sacrificial anodes had both a dimension of 30cm length x 5cm width x 5cm thickness. However one of the zinc sacrificial anodes was prepared by rolling an expanded zinc sheet with a total anodic surface area of 3300 cm^2 .

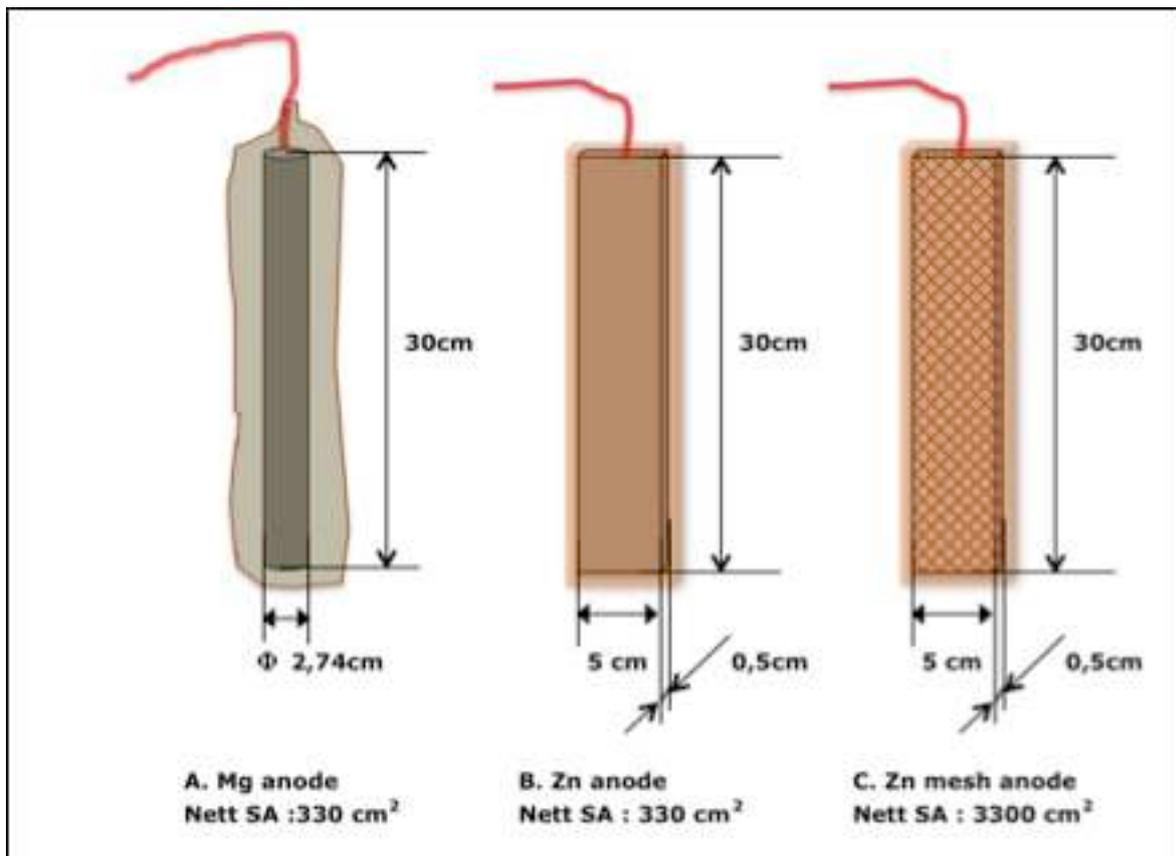


Fig. 1 sketches of the anodes :

- A. Magnesium anode with 300 cm^2 surface area in traditional backfill.
- B. Zinc anode with 300 cm^2 surface area coated with appr. 2mm electrolytic paste and covered with a cotton protective bag.
- C. Zinc mesh anode with 3300 cm^2 surface area coated with 2mm electrolytic paste. Also, the mesh was filled up with the paste to have all anodic surface area covered.

- Three uncoated steel mesh samples with a dimension of 300mm x 250mm x 1mm were prepared and degreased.

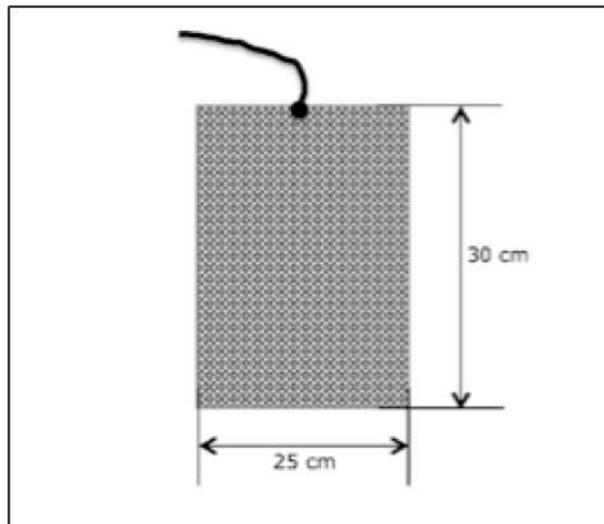


Fig. 2 Cathode : steel mesh sample of 30cm x 25cm.

- Three containers with a dimension of dia 45cm, height 35cm, a volume of 55 L, and filled with sand with 0,1% Cl^- (m/m) with a specific resistivity of 500 Ωm .

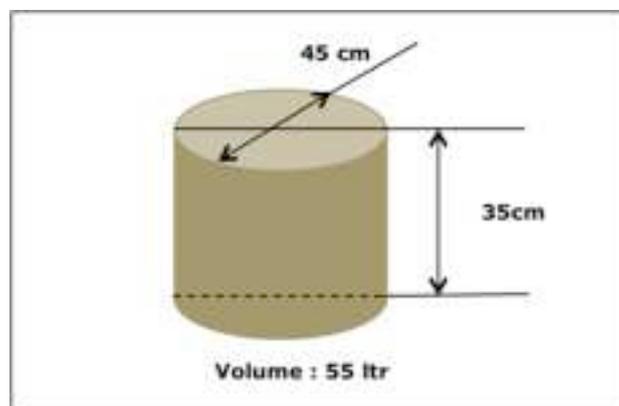


Fig. 3 The dimensions of the 55 ltr container filled with sand.

The anodes were placed together with the steel mesh plates in the containers with a distance of 30cm from each other and filled with sand. By use of a zero-resistance-amp-meter (ZRA) the current output of the anode was measured over time. An LCR-meter was used to measure anode to cathode resistance (impedance) over time at a frequency of 120 Hz.

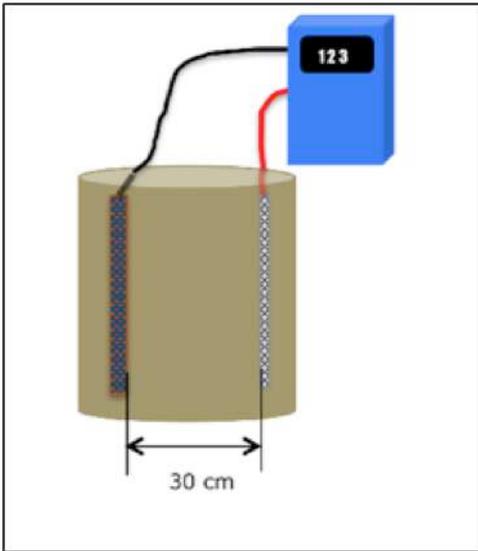


Fig. 4 The distance between anode and the cathode.



Fig. 5 Picture of one of the three experimental set-ups.

Results

The results can be found in the graphs below of which the first graph in Fig. 6 shows the anode output over six months measured by a zero resistance ammeter and Fig. 7 shows the anode / cathode resistance over the same period measured with an LCR-meter at a frequency of 120 Hz.

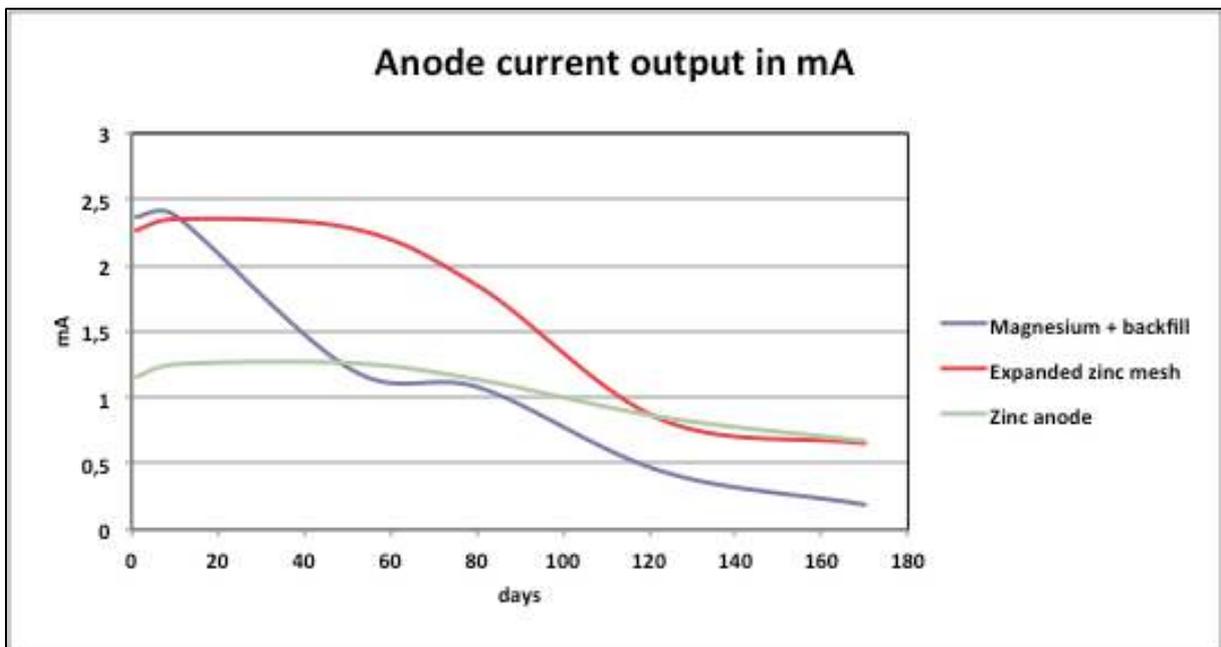


Fig. 6 Anode current output over a period of 6 months.

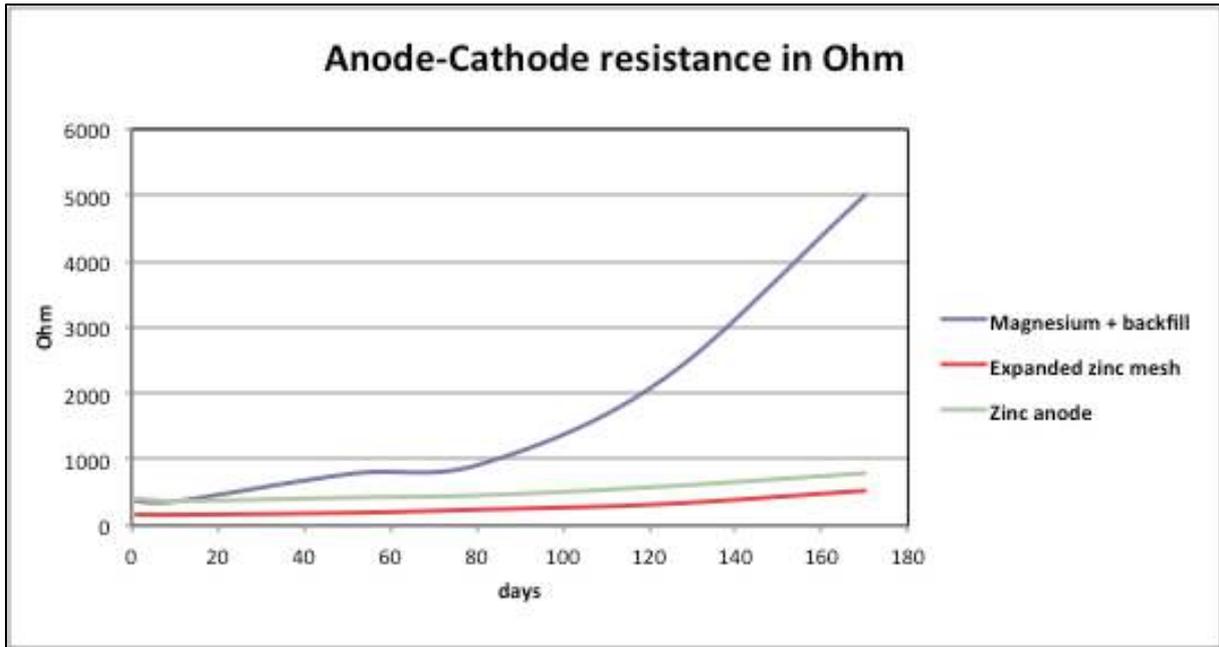


Fig. 7 Anode-Cathode resistance over a period of 6 months.

Discussion

Fig. 6 shows the current output of all three anodes produced during the six months of service under experimental conditions. The results indicate a relatively high initial current output of the magnesium anode with a maximum value of 2,38 mA after 10 days of service which started to reduce to almost half of this value within 60 days. Subsequently the current output remained stable for about 20 days and started to reduce even further to values of around 0,2 mA at the end of the experiment after 170 days.

The inversely proportional relationship between current and resistance of the magnesium anode can be clearly seen when comparing the current output in Fig. 6 with the measured resistance in Fig. 7. The measured resistance proceeds in exact the opposite direction compared to the current output of the magnesium anode. The resistance is measured with an LCR meter, so actually it is not the resistance but the impedance which is measured at a frequency of 120 Hz. The reason for using an alternating test signal is to eliminate the polarisation affects. These measured values are not ohmic resistances, so care should be taken when using these values for calculation purposes as they may vary up to 20% compared to the real ohmic resistance of the galvanic system.

A possible reason for the strong increase of the resistance of the magnesium anode after approximately 80 days of service may lay in the build-up of passivating surface layers by the backfill. Research by Song et al ^[1] discovered an important role of partially protective surface films during the dissolution of magnesium in chloride and sulphate solutions. This may confirm the behavior of the magnesium anode which also can be seen on the pictures taken from the anode after six months of service in Fig. 8 and 9. For that reason Gummow ^[2] recommended from an efficiency perspective packaged zinc anodes as a better option under some application conditions than backfilled magnesium sacrificial anodes. He indicated that

evaluations of high potential magnesium alloys from various suppliers using the ASTM G97-89^[3] test method showed widely variable efficiencies resulting in service lives less than design calculations would predict due to operating factors.



Fig. 8 Magnesium anode after 6 months of service



Fig. 9 the magnesium anode was partially covered with a thick, well-adhered, scale.

Quite remarkable is the exceeding initial current output of the zinc anode fabricated from expanded mesh compared to the standard zinc anode. Although the resistance of this anode is less than half the value of the standard zinc anode, the current output after approximately 60 days both slowly equalise. Surprisingly the reason for this slow current reduction is not seen from the resistance curve of this anode and should most probably be found in the current demand from the steel cathode. Generally these kind of experiments are performed with low anode/cathode surface area ratios preferably 1/20^[4]. Increasing the internal anode surface area will change the anode/cathode surface area and may affect the current output of the anode specifically when the cathode starts to passivate and current demands will reduce. The use of an increased cathodic surface area would certainly have been a better option for this part of the experiment in which an increased anode surface area is studied.

As indicated above the total surface area of the "expanded mesh" zinc anode is 10 times the surface area of the standard zinc anode, 330 cm² versus 3300 cm². The substantial increase of surface area is accomplished by increasing the internal surface area within the same exterior dimension of the zinc anode. As a result we measure a lower resistance, 163 versus 413 Ohm. Mathematical considerations show a natural logarithmic (ln) relation between anode surface area and anode grounding resistance^{[5][6]} as can be seen in Fig. 10.

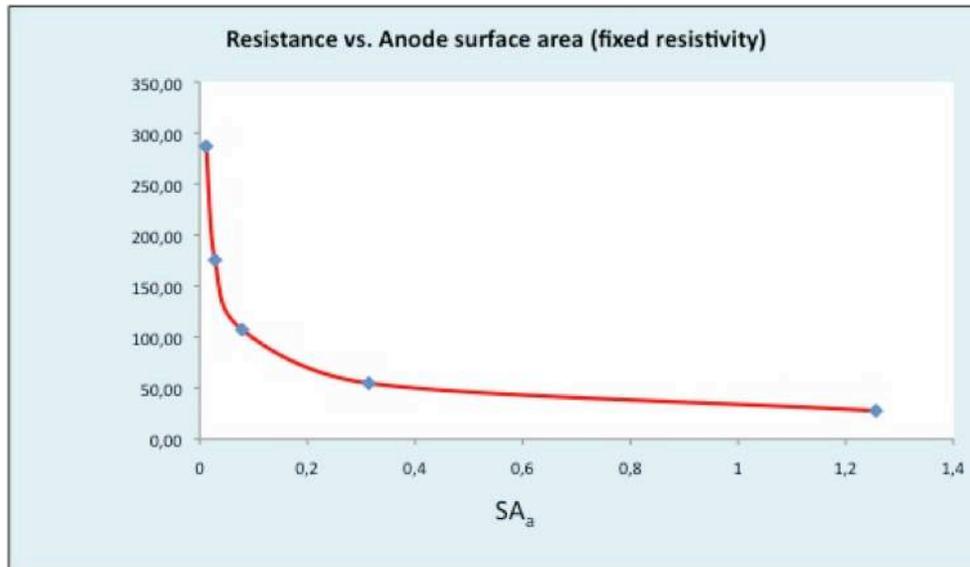


Fig. 10 Graphic presentation of the relation between anode grounding resistance and anode surface area.

In many CP design recommendations and general literature about cathodic protection of steel structures and steel in concrete structures, anode/cathode surface area ratios and limiting anode current densities are mentioned as points of particular interests due to the effect on the service lives of anodes. Generally the effect of current densities on service life of anodes is a straightforward calculation through Faraday's law. However, the relation between anode performance, corrosion control and anode/cathode surface area ratios concerning galvanic anodes is more complex [7].

This relation can be explained by using the "mixed potential theory". Fig. 11 shows E-log I polarisation curves of an iron and a zinc electrode in an electrolyte. When electrically connected, the potential measured will be the point of intersection between the two curves and projected on the potential-axis which is the mixed potential of the two electrodes. This type of diagram is inadequate to reflect all the effects of galvanic coupling, as it deals with current density, and therefore is not able to show the effects of different surface areas between anode and cathode.

Fig. 12 is actually re-drawn by not using current density but total current on the log I-axis. This diagram, however, is able to show the effect of changing the area of one electrode relative to the other. It shows that if the cathode area increases, the potential becomes less negative so less polarisation of the cathode/structure although with an increasing current output.

This phenomena is well noticed during experiments performed in the field with sacrificial anodes specifically applied in reinforced concrete structures due to the relatively small anode dimensions [8] [9]. The small surface area of these sacrificial anodes are barely able to polarise the steel reinforcement of the concrete as its surface area is many times smaller than the surface area of the steel reinforcement. A simple solution to overcome this issue is to apply anodes with increased surface area.

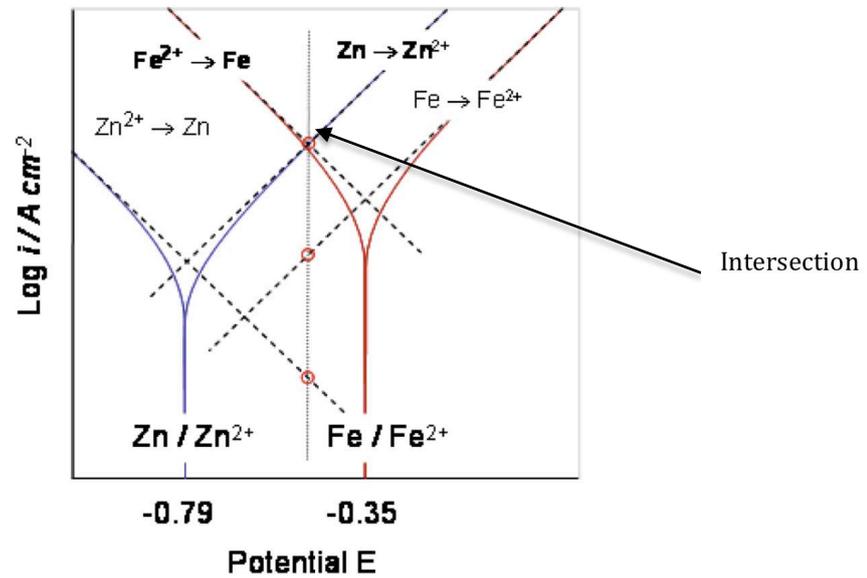


Fig. 11 E-log I polarisation curves of Fe vs. Zn by using current densities.

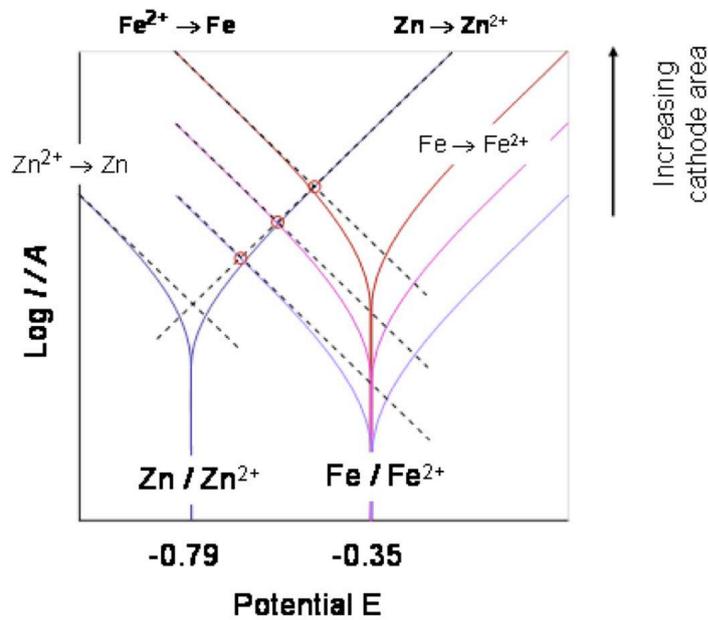


Fig. 12 E-log I polarisation curves of FE vs. Zn by using total current.

The electrolytic paste or coating is of a flexible compound requiring no additional humectants, deliquescent or backfill to keep the zinc anode active. The coating provides a number of important properties to assure adherence and flexibility between the anode and surrounding environment in which it is embedded. The electrolytic coating is comprised of an ion conductive water based acrylic binder, a pH adjuster, an inert filler material to modify viscosity and tackiness as used in caulk products, an alcohol based water binder and zinc activating agents.

The electrolytic coating chosen to be used in this experiment was the coating which performed the best as a result from the potentiodynamic polarisation scans which were compared and qualified as can be seen in Fig. 13.

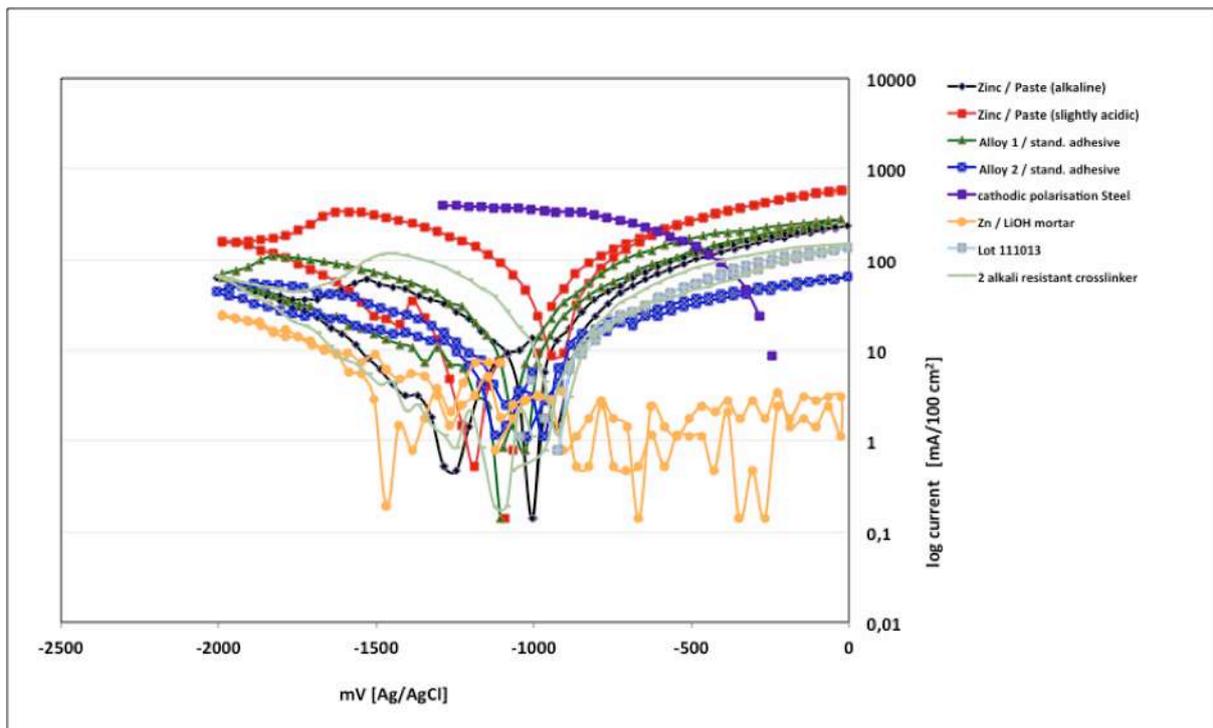


Fig. 13 Potentiodynamic polarisation scans (sweep rate : 0,1667 mA/sec) of several prepared pastes applied on zinc.

The paste was applied directly on the zinc surface with a thickness of two mm. The zinc anode fabricated from expanded mesh needed more paste due to its internal open structure of the anode. The openings in the expanded metal patterns needed to be filled with the paste to ensure electrolytic continuity.

After six months of service both zinc anodes still looked unblemished with no indication of scale-formation or any passivation layer (Fig. 14 and 15).



Fig. 14 Zinc anode after 6 months of operation.



Fig. 15 Zinc anodes showed no sign of scale formation.

Conclusions

- ❖ This experiment has shown a strong increase in resistance during service by the magnesium anode most probably due to the build-up of passivating surface layers by the backfill.
- ❖ Increasing the anode surface area will increase the anode current output, as the increased anode surface area will reduce the anode resistance.
- ❖ To improve the quality of this experiment, an increased cathodic surface area should have been used.
- ❖ Although both zinc anodes coated with the paste showed good performance during six months of service and could easily compete the performance of the magnesium anode, it is recommended to extend a similar test period preferably in situ for at least twelve months.
- ❖ Both zinc anodes showed no signs of scale formation or any sign of passivation during this experiment.

Reference

- [1]. The anodic dissolution of magnesium in chloride and sulphate solutions. G. Song, A. Atrens, D. St. John, X. Wut, J. Nairn. Corrosion Science, Vol. 39, No. 10-11 pg 1981 - 2004, 1997.
- [2]. Why are you still using magnesium anodes ? R.A. Gummow. XII National Conference "Corrosion Measurements in Electrochemical Protection" 2012 Jurata, Poland.
- [3]. ASTM G97-89 'Standard Test Method for Laboratory Evaluation of Magnesium Sacrificial Anode Test Specimens for Underground Applications', ASTM, 1989.
- [4]. Recommended Practice, Det Norske Veritas, Report DNV-RP-B401, Cathodic Protection design, October 2010. Page 33.
- [5]. Handbook of Cathodic Corrosion Protection, 1997, W. von Baekmann et al. Table 24-1, Page 538.
- [6]. NACE, Cathodic Protection Training and Certification, Level 4 Course Manual, November 2003. Chapter 2 Factors Influencing CP design.
- [7]. Electrochemical techniques in corrosion science and engineering, Robert G. Kelly, John R. Scully. Chapter 2, Page 52. ISBN 0-8247-9917-8 .
- [8]. Galvanic point anodes for extending the service life of patched areas upon reinforced concrete bridge members. A.A. Sagues, University of South Florida. Final report to Florida Department of Transportation.
- [9]. Evaluation of point anodes for corrosion prevention in reinforced concrete structures. M.Dugarte, A. Sagües. NACE Report 07304.