Galvanic Cathodic Protection System Complying With Code Based Protection Criteria

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Synopsis: Impressed current cathodic protection of reinforcement in concrete structures is a technique developed over the last 40 years and today is a well accepted method for repair and prevention of corrosion. More recently galvanic anodes systems have been used to provide a similar method of corrosion control but with the benefits of limited wiring. Such systems have the potential for wide spread use on smaller areas or elements where the complexities of impressed current systems make them unwieldy. Issues when using zinc galvanic anodes in or on concrete are assurance that corrosion protection criteria are achieved, prevention of the zinc passivation and use of a universal design life assessment method.

The paper describes a review of some galvanic anode systems used on concrete. Limitations of the systems are discussed in relation to ease of application, assurance of corrosion protection and durability of the systems. A method of assessing the design life is also provided. Particular attention is given to a new type of galvanic anode systems. Zinc Layer Anodes are zinc sheet bonded to the concrete surface using a specifically developed combined adhesive and anode paste applied to the sheet at the time of manufacture of the anode.

Keywords: Concrete, durability, chloride, carbonation, cathodic protection, repair, galvanic anode

1. Introduction

Impressed Current Cathodic Protection (ICCP) systems are not without their problems but over the last 40 years they have been found to be suitable for a wide range of concrete structures. In the USA over 500 bridges(1) have had ICCP applied. Chirgwin(2) reports that *"RTA has eight ICCP systems in operation However due to the relatively high cost of ICCP and the high demand on internal resources the number of ICCP systems that can be commissioned is limited … Delay in implementing ICCP leads to an increase in the level of concrete deterioration .. Apart from the structural implications … increases the cost of ICCP installations due to a greater volume of concrete patching."* Because of the economic issues with ICCP RTA are considering the use of lower cost galvanic anode systems for holding repairs. In this paper the development of various galvanic anode CP systems are considered with the objectives of providing a better understanding of the systems available and of indicating a route for developing a design requirement for galvanic systems.

2. Development of Galvanic Anode Cathodic Protection for Concrete

The wide spread acceptance of ICCP systems serves to show that use of CP systems for concrete are eminently practical. However, ICCP systems may not be practical for protection in many areas, e.g.:

- where resources are not available for ICCP system (e.g. RTA situation)
- where ICCP systems are very expensive (e.g. for small projects or projects with many isolated areas)
- on projects where electrical systems are not ideal (e.g. hazardous area)
- in areas where wiring is not practical (e.g. many mine site areas)
- where localized protection is required (e.g. at corners, joints or areas of localized low cover)

For steel structures sacrificial zinc anodes are used extensively and they form a logical extension for corrosion protection on reinforced concrete structures. In this paper the development and current status of galvanic anodes is discussed. In particular criterion for assuring protection is achieved are discussed and a method of designing galvanic systems is outlined.

3. Scientific Basis for Cathodic Prevention and Cathodic Protection

Page(3) describes cathodic protection in relation to his simplification of Bertolini's(4) domains of electrochemical behavior of steel in concrete (Figure 1). Using Figure 1 three types of protection can be derived:

a) Cathodic Protection: For repair of structures corroding due to chloride ingress the reinforcement is polarized from 'Pitting' to 'Pitting Unstable' to provide protection but even potential movement in this direction reduces the corrosion rate.

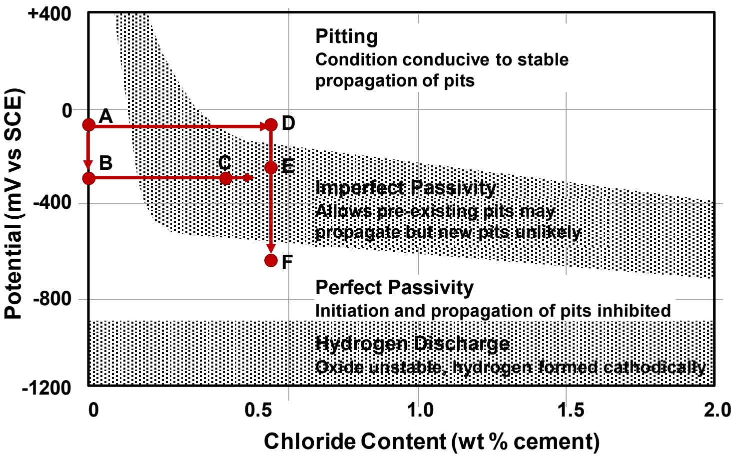
b) Cathodic Prevention: In new structures where chlorides have not caused corrosion activation only a small polarisation is required to put the reinforcement in the 'Imperfect Passivity' domain. Then, even as chloride levels increase, pits will not form.

c) Incipient Anode Prevention: The area around a repair is likely to have some chloride but pitting will not have commenced as reinforcement in the repaired area previously acted as the anode so pitting corrosion has not commenced. Such areas can still be protected by a small shift in potential to the Imperfect Passivity Zone.

Figure 1 : Domains of Electrochemical Behaviour of Steel in Concrete

A-B-C: Cathodic prevention polarizes the reinforcement from A to B so that as chloride levels increase to C the reinforcement does not corrode.

A-D-E-F: Chloride ingress takes the reinforcement from A to D to E. At E the pits continue to corrode. Application of cathodic protection takes the reinforcement to F where it is protected.



This basic understanding of corrosion protection given by Figure 1 is useful when considering the objectives of different galvanic anode systems. Key aspects are:

1) A major benefit of using galvanic anodes such as zinc is that they cannot polarize the steel sufficiently to take it to the hydrogen discharge range.

2) In cathodic prevention systems only a small polarisation is required to insure the steel stays protected while in a cathodic protection systems higher polarisation is required. European standard EN12696 indicates that current densities for cathodic prevention range between 0.2 - 2.0 mA/m^2 compared with 2 - 20 mA/m^2 for cathodic protection on uncoated steel in concrete.

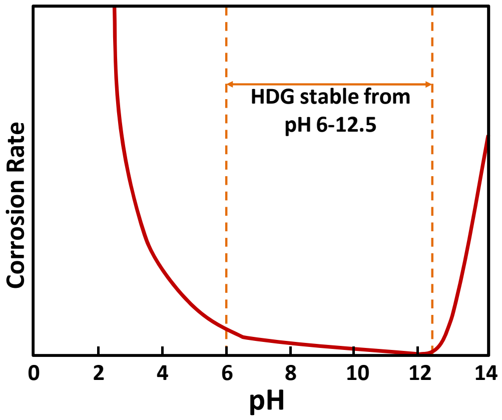
3) Current drawn to protect steel in concrete depends on the potential difference between anode/cathode and anode/cathode resistance. Hence the current drawn than can be quite accurately estimated by Ohm's law : $I = V / R$.

Sagues(5) models the throw that can be expected from point anodes with time. The model shows that as the steel density and anode spacing increases the throw decreases dramatically. For a depolarisation of 150mV, anodes at 0.5m spacing and heavy reinforcement densities the throw would reduce from 200mm to 80mm after only a year and would drop significantly with time after that. With a depolarisation of 100mv and light reinforcement the throw would reduce from 400mm to 300mm after one year.

4. Use of Zinc as the Galvanic Anode

Anodes protect the steel reinforcement as they have a lower natural potential than the steel and hence a potential difference is set up between the anode and steel such that the anode corrodes rather than the steel. Zinc is often used as the anode as it has a small manageable corrosion expansion and an ideal potential that is sufficient to polarize the steel but not so great that it can cause hydrogen evolution. However zinc anodes passivates at the normal pH of concrete (Figure 2) and this made early attempts in the 80's to use perforated zinc sheet in concrete unsuccessful(6). Since then various methods of maintaining the zinc activity have been developed. These include use of lithium nitrate based mortars to keep the pH above 13.5 and chloride and sulphate low pH based pastes.

Figure 2 : Stability of Zinc In an Alkaline Mortar



Passivation of the anode doesn't only occur due to the environment. Metal impurities in the zinc lead to low anode efficiency. Hence the iron content of the zinc has to be limited as much as possible to decrease local cathode activity on the anodes' surface.

A principle question with zinc anodes is whether they produce the protection potential for cathodic protection and if they do what the life of the anode will be based on its consumption rate. Impressed current systems can operate successfully at current densities in excess of $20 mA/m^2$ (Page[3]) and it can be calculated that some zinc systems would last only around 5 years at that density (Page[3]). It is important to recognize that zinc anode systems successfully used for Cathodic Prevention, where current densities of 1-2 mA/m^2 may apply, may give very short lives where a high current density necessary for cathodic protection is supplied.

5. Types of Sacrificial Zinc Anode

Zinc being the obvious sacrificial material means that many companies have developed sacrificial anode systems. Some of these developments are discussed below as they give a good guide to the key aspects of a galvanic anode CP system.

Distributed Anodes

Zinc sacrificial anodes used in steel reinforced concrete were studied in the 70's and 80's by scientists like J.B.Vrable(7). Reports from that period indicated that they recognised the interaction between the water-binding ability of deliquescent additives and anode performance as well as problems caused by the expansion of the corrosion products which could be solved by implementing some porosity in the anode or surrounding material. In the same era other scientific publications reported on zinc anode systems placed on concrete or in concrete grooves using porous Portland cement mortars as a stabilizing backfill and perforated zinc anode sheets bedded on porous materials to keep high moisture contents. It was found that factors like temperature, moisture and salt content played an important role in functioning of the anodes.

In the mid 90's galvanic anodes for embedment in concrete suitable for cathodic prevention of incipient anodes were developed(8). These used a small puck of zinc embedded in a Lithium based mortar. The lithium gave a pH in excess of 13.5 and at that pH the zinc remains active and corrodes sacrificially to the reinforcement. By placing the anodes around the edge of repairs (i.e. close to the incipient anode areas) and because only low current was required to give the small polarisation needed for the protective current these were sufficient. The manufacturers recognised that the system was not suitable for cathodic protection due to the current output limitations.

The original system has been used extensively and later systems with higher anode areas and masses have had many trials. There is limited information on the anodes themselves, presumably for commercial reasons, and the number of anodes required in a system is based on the manufacturers guide. This lack of a fundamental design method prevents a scientific approach to the rate of consumption of anodes. For example Brown(9) undertook a study for the Virginia Department of Transport and reports that even in a low current density cathode prevention system anode consumption was around 5% in 130 days. Even though currents decrease over time the high consumption at low steel current densities indicates a relatively short life. Considering repairs are often only expected to last 15-20 years this may not always be an issue but if lives unexpectedly slip to 10 years or less then the maintenance cost could be unacceptably higher, particularly given that these anodes are embedded and not simple to replace.

Another issue is the ability of the anodes to sufficiently polarize corroding reinforcement in a full cathodic protection arrangement. Sagues(5) undertook laboratory and field trials and found that *".. point anodes of this size and at the placement density used, and for the amount of steel in the slabs, are not likely to provide substantial levels of cathodic protection of an already corroding bar assembly."*. He did note that once the corroding bars were switched out of the circuit the anodes did provide 100mv depolarisation values on the passive steel.

There are various types of distributed anodes available and their performance is dependent on surface area, zinc mass and activation system. The issue of throw is a significant consideration and a model such as Sagues's would be a useful design tool if manufacturers were compelled to give accurate product information of a defined nature (e.g. surface area and polarisation potential curves for different anode:cathode ratios and electrolyte resistivity).

Thermally Sprayed Zinc Anode

Another system developed in the mid 90's was thermally sprayed zinc. In these systems zinc is sprayed onto the concrete surface to act as a sacrificial anode. The issue of passivation of the zinc in contact with the concrete is an obvious potential problem. Gawedzinski(10) reports on trial systems installed on bridges and notes *".. potential surveys indicate the systems are not protecting the steel. It appears the anodes do not develop enough current ..".*

Since then the sprayed zinc systems have been developed further, considerations has been given to achieving high initial bond, breakdown of bond due to acidification of the interface, quality assurance of application and how the zinc stays in contact with the concrete as the surface corrodes. Covino(11) found that the systems can work with relativity long design lives particularly in a cathodic protection mode where currents are low. In Cathodic Protection situations the system could give high current outputs (>10mA/m^2).

Thermally sprayed zinc systems can be effective but they require specialist application skills, a strong understanding of the key success factors and a high level of quality assurance. Although significantly less resource hungry than ICCP they still demand significant resource and are not really suited to use on small areas due to issue with stop/start application.

Early Hydrogel Zinc Sheet Anode

In the late 90's a zinc sheet cathodic protection system that could be bonded to the concrete surface and remained active due to the hydrogel was introduced. The galvanic protection worked very well due to the high surface area and maintenance of zinc activation. The system was tested on three sites by the Illinois Department of Transport. Gawedzinski(10) concluded that *".. the system did conform to the NACE specification of a 100mV depolarisation over 4 hours."*

Unfortunately the system had three problems and it seems only one product batch was made (used for several CP systems in the US and Europe) before the system was discontinued:

- production difficulties as the gel jambs the production plant
- the high pH of the hydrogel necessary to maintain the zinc activation led to the formation of a zinc hydroxide layer that passivated the anode under certain conditions.
- some failures due to the hydrogel in locations of water leakage. Gawedzinski notes that in the Illinois trials *"…where the anode was placed on the outside of the fascia beams in areas exposed to leaking joints, it was beginning to separate from the face..".*

Modern Zinc Sheet Anode

After the early zinc sheet was discontinued a two year R&D project was undertaken by CorrPRE. Working in conjunction with a specialist zinc sheet manufacturer the issues were resolved by 2002. The ZLA comprises a zinc sheet backed with a combined adhesive and activator paste (Figure 3). The adhesive is protected by a paper that is pulled off when the zinc sheet is to be applied.

Figure 3 : Modern Zinc Sheet Anode

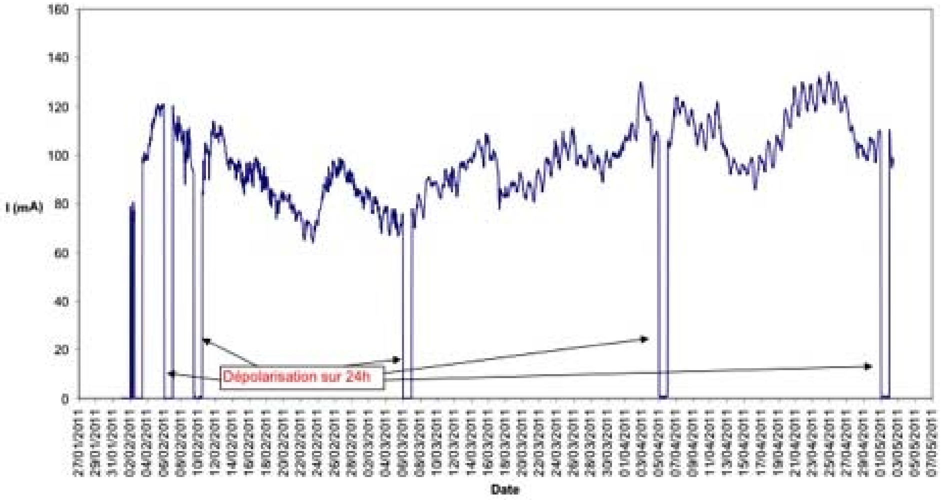
a) Anode Construction b) Rolls of Anode Packed for Shipment c) Anode Application

Solutions to the production and pH issue remain confidential. However it is noted that a slightly acidic pH base is used but other factors also account for the high output. The issue with water contamination was resolved by incorporating suitable waterproofing systems into the system design.

Table 1 : Depolarization potentials (EN12696) For Various Reference Cells For Viaduct

No	Zone	Re Type	Location	Depolarisation (mV @24hrs)					
				10/12/10	15/12/10	22/12/10	6/2/11	6/3/11	1/5/11
9	4	AMO 5	Pre-stressed Beam Nr 1	182	182	161	172	182	161
10	4	ERE 18361	Pre-stressed Beam Nr 1	194	194	152	180	179	172
12	4	ERE 18380	Between Consoles	147	254	170	141	161	159
13	4	AMO 7	Between Pre-stressed Beams	209	191	192	189	197	182
14	4	ARE 18362	Top Section Column	110	104	128	104	119	119
15	4	AMO 6	Console 1	100	97	118	98	110	107
16	4	AMO 8	Corbel	254	257	202	211	213	188

Figure 4: Total Current Out Put for Viaduct



Monitoring results for a modern zinc sheet system for projects are out lined below.

In the first case 46m^2 of ZLA was installed on pre-stressed beams of a viaduct of the motorway B9/E19 in Brussels in May 2010. Depolarisation potentials and current outputs as monitored by an independent consultant are shown in Table 1.

The results show that the current output varies depending on the ambient conditions. However the depolarization at 4 hrs achieves the requirements of EN12696 even in this structure where the reinforcement density in the concrete was high and also at point no. 15 where the reference electrode (AMO 6) was located almost 50cm away from the ZLA.

In the second case sixty balcony supports for offices in Rijen - Netherlands had 1.8 sq.m of ZLA per applied to each support in 2008. Results for three measuring points as monitored by an independent consultant are shown in Table 2.

Table 2 : Depolarisation Results for Offices in Rijen, Netherlands

No	Point	Start up17/4/2008		In service on 10/3/2010			
		Time after start up	Current (mA/m^2)*	On Potential (mV)	4hr Off Potential (mV Ag/Ag Cl)	Depolarisation (mV)	Current (mA/m^2)*
1	Blok 3	10min	13.8	-489	-275	214	3.9
2	Blok 4	14min	22.2	-577	-315	262	4.4
3	Blok 5	8 min	8.3	-610	-320	290	3.6

*Based on applied area of 1.8m^2

The results show that the depolarization required for cathodic protection by EN12696 was easily achieved and the anode current density after 2 years was within the expectation for the ZLA.

6. Codes

AS 2832.5 governs the use of cathodic protection of steel in concrete. It recognizes the European standard EN 12696 on the same topic. Both codes give the same alternative protection criteria, i.e.:

- 'instant off' potential more negative than -720 to -1100mv (-770 to -900mv if prestressed) with respect to a Ag/AgCl/0.5M KCl electrode.
- a 24hr potential decay of 100mV min.
- a long term potential decay of 150mv min.

These are proven values for cathodic protection and although some manufacturers suggest that they are too onerous, less onerous values have not been proven. Hence these values should be observed for cathodic protection systems using galvanic anodes. Alternative protection requirements are suitable for galvanic prevention.

7. Galvanic Anode Research Results

Zinc galvanic anodes have been used for cathodic prevention in concrete for the last 15 years and for cathodic protection (higher reinforcement current density required) for the last 10 years and the following research is of value in assessing the current densities required to give protection.

Sergi(12) provides data on 13 structures where zinc anodes in a lithium nitrate based mortar were embedded in concrete and used for corrosion prevention and cathodic protection. Small anodes were a plane zinc disc in an alkaline mortar with no attempt to increase the zinc surface area. The larger anodes had a series of thinner zinc discs in an alkaline mortar. Sergi lists the anode type for the cathodic prevention and the surface area of the zinc is around 3400mm^2 for a zinc weight of 0.06kg i.e. 60,000mm^2/ kg. Some of Sergi's results shown in Table 3 were difficult to estimate due to unclear anode to cathode surface area ratios.

The anode current density does not change markedly between cathodic prevention and cathodic protection and any increased performance arises from the increase in anode to cathode surface area ratio. Hence the data provides some guidance on current densities that can be used for design of zinc anodes in Lithium nitrate based mortars. Given the low cost of increasing protection relative to the high cost (actual cost plus public cost) of failure it is reasonable to require a very low likelihood of premature failure. This likelihood is difficult to assess as the current density probability distribution is not normal and the data is limited. However as derived from the data in Table 3 current densities for design of these discrete anodes could be based on those shown in Table 4.

Table 3 : Corrosion Current Using Embedded Zinc Anodes

	Corrosion Prevention			Cathodic Protection		
	Anode current density (mA/m^2)			Anode current density (mA/m^2)		
	Yr 1	Yr 2	Yr 3	Yr 1	Yr 2	Yr 3
Mean	33	22	10	45	27	14
+95% CI	132	92	31	106	51	26
Max	131	94	26	87	40	18

Table 4 : Anode Current Densities (mA/m^2)

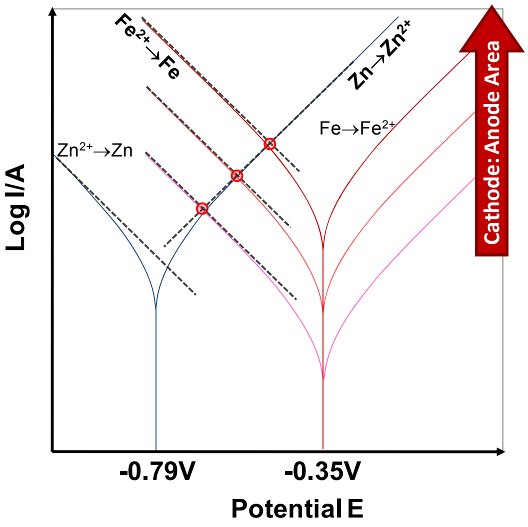
Year	Discrete Galvanic Anodes	Surface Layer Anodes
1	50	20
2	30	5
Remainder	10	5

For Zinc Layer Anodes in a slightly acid activation paste the current will become controlled by oxygen diffusion to the cathode and the higher anode surface area will lead to lower anode current densities. The authors have found that anode current densities given in Table 4 are approximately appropriate but values vary depending on the electrolyte around the cathode, particularly its chloride content. This serves only to indicate that different anodes are likely to have different anode current densities.

For a given puck size the surface area of zinc can be increased by around 2.5 times by sculpting the zinc block within practical limits. This enables a high zinc surface area per kilogram of zinc which, assuming the current density on the zinc is the limiting factor in the EMF, produces a higher current /kg of zinc. Whilst this is positive for economic polarisation of the reinforcement (the same effect can be achieved without sculpting by simply increasing the number of anodes) care has to be taken in design to ensure there is sufficient zinc to maintain protection over the design life. Sculpted anodes have a surface density of around 90,000 mm^2/kg zinc compared to 550,000 mm^2/kg zinc for zinc sheet applied to the surface. With zinc sheet the high surface area of zinc and the anode paste characteristics minimises the limitation of anode current density in providing sufficient current to polarize the reinforcement in cathodic protection projects.

Sergi(12) states that increasing the anode area in each anode and the number of anodes led to the increase in current produced. Unfortunately the area of zinc in the anodes is not given and this cannot be confirmed. Certainly the current density on the reinforcement was increased by a factor of 5 when the anode:cathode area increased.

Figure 5 : Zinc : Iron Polarisation Curves



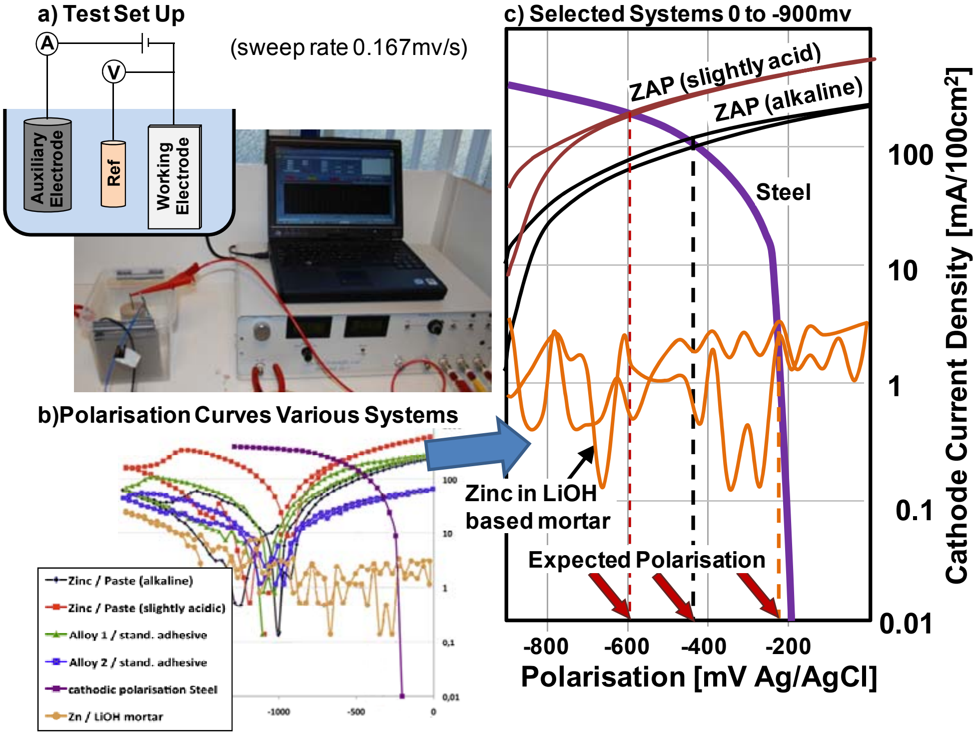
As discussed above the problems generally encountered with sacrificial anodes - and it doesn't matter whether they are applied in reinforced concrete, soil or seawater - is a situation in which the anode : cathode surface area is too small so that the sacrificial anode is not able to provide enough polarisation to the structure while the current provided by the anode remains virtually constant. Such a situation can be clearly explained through the so called "mixed potential theory". Figure 5 shows the effect of changing the area of one electrode relative to the other, and if the cathode area increases, the potential of the anode becomes more positive so less polarisation of the structure is obtained.

This phenomena is well noticed during experiments performed in the field with discrete sacrificial anodes and applied in reinforced concrete due to their relatively small dimensions. The small surface area of the sacrificial anodes are barely able to polarize the steel reinforcement of the concrete as its surface area is many times smaller than the surface area of the reinforcement. That is not to say that discrete anodes cannot work for cathodic protection only that a good understanding of the polarisation achievable based on anode:cathode surface area and polarizing potential is required for design and this information is often lacking**.**

Another way to assess the performance of galvanic anodes is by use of a widespread accepted technique called ‘Cyclic Voltammetry’ (CV). CV is used to study the electrochemical properties of an analyte in solution and provides significant useful information regarding the corrosion mechanisms, corrosion rate, and susceptibility of a metal to corrosion but is also used to judge the electro-chemical performance of different electrolytes with a fixed metal system.

The test set up is shown in 6a. The working electrode (anode system under consideration) and the auxiliary electrode (platinized titanium plate) are immersed in an electrolyte (thickened demi-water) together with a reference electrode. Comparison of an anode pastes performance is relatively simple as the anode area and auxillay electrode remain constant. Comparison between anode types becomes more difficult as some assumption about the anode : cathode area and the effect of the electrolyte resistivity has to be incorporated into the analysis.

Figure 6 : Potentiodynamic Polarisation Curves of Zinc in Different Electrolytes (Giorgini [10])



a) Test Set Up

b)Polarisation Curves Various Systems

c) Selected Systems 0 to -900mv

Where comparisons are needed on a job by job basis the electrolyte resistivity and anode : cathode ratio of each system would need to be representative of the project. However, for general comparison of anode performance it might be possible to develop some standard arrangements that represent common situations.

This cyclic potentiodynamic polarisation technique for corrosion studies was introduced in the 60s and refined during the 70s into a fairly simple technique for routine use. In this technique, the voltage applied to a half cell system (anode or cathode electrode and electrolyte) under study is ramped at a continuous rate relative to a reference electrode using a potentiostat. The voltage is first increased in the anodic or noble direction (forward scan). At some chosen current or voltage, the voltage scan direction is reversed toward the cathodic or active direction (backward or reverse scan).

As both metals (zinc and steel) in a sacrificial CP system must be at the same potential, the corrosion potential of the two metals is given by the intersection of the anodic and cathodic polarisations. This intersection point gives the polarized potential and current density which will be measured in practice.

CV has been used in the development of the CorrPRE anode systems. By changing slightly the formulation of the electrolyte any alteration of the anode system performance was determined. Results are illustrated in the Figure 6b for various systems throughout the voltage cycle and show a large variation in polarizing potential. Figure 6c is an enlargement of Figure b over the range 0 to -900mv for selected systems. It shows the

- low polarisation achieved using zinc anodes in a lithium based mortar (sufficient for cathode prevention but not ideal for cathodic protection this case)
- significantly higher polarisation when the Zinc Anode Paste (ZAP) composition changes from alkaline to slightly acidic

high polarisations (sufficient for cathode protection) achieved with the slightly acid ZAP.

8. Design Life Calculation Methods For Galvanic Anodes

Zinc Consumption Rate

One aspect of the life of a zinc anode is defined by the rate of consumption of the zinc and can be calculated using Farday's law. The anode current density for a given anode material/anode paste combination depends on the corrosion activity of the cathode (Figure 1) and this can be represented by the chloride content at the steel surface. Hence, the values used for the Zinc Layer Anode are determined by the chloride concentration at the face of the reinforcement based on corrPRE's experience. Other values will apply for other anode systems.

Alkali Silica Reaction (ASR)

The potential field set up by cathodic protection means that sodium and potassium ions are drawn to the rebar and the concentration effect was considered a risk for alkali silica reactions. However the risk has been found to be insignificant if the current is uniform and less than 20mA/m^2 (Sergi & Page[14]). Where there is a risk of ASR then a lithium treatment can be applied to the concrete as part of the repair process.

Chloride removal

The potential field also leads to chloride ions being drawn to the anode. This reduces the chloride at the reinforcing combined with a re-alkalization leading to a lower polarisation and current draw. For surface anode systems chlorides arriving at the surface may become apparent as salts. This can be an issue if the surface anode has not been designed to absorb or discharge these products.

9. Conclusions

There are models for assessing the current throw and anode consumption rate for galvanic anode systems however these are rarely used and there is no industry standardization on specification of anode parameters that would enable modeling of different anodes. Standard performance details for all galvanic anode systems would enable modeling for generalized and specific projects and would enable users to select the anodes to use based on a scientific and economic basis. The paper shows how cyclic voltametry can be used to compare components within a galvanic system for optimization purposes and points to a possible way of extending the system for a more general comparison.

Galvanic anodes provide a useful means of providing corrosion protection. Small discrete anodes are suited to cathodic prevention while anodes with a larger anode:cathode ratio and suitably designed activation system can be used for cathodic protection. Depending on the polarisation achieved and the zinc mass it is quite possible to obtain design lives of galvanic anode systems of 20+years.

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