



Service life estimation, failure mechanisms, and specifications of galvanic anodes for corroding reinforced concrete structures

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Abstract Cathodic protection using galvanic anodes is a proven technique to control or prevent corrosion of steel in reinforced concrete structures. However, huge variations have been observed in the properties of various galvanic anodes available in the concrete repair market and their resulting performance. This work assessed the performance of five commercially available galvanic anodes using an earlier developed Galvanic Anode Performance (GAP) test. In addition, a methodology to estimate the guaranteed minimum service life (SL_{min}) of galvanic anodes in concrete systems exposed to specific environmental conditions is developed. This methodology involves the determination of electrochemical capacity (i.e., total electrical charge drawn) of galvanic anodes and the corrosion rate of galvanic anodes using potentiostatic scans. It was found that the average SL_{min} of the five anodes tested under severe laboratory exposure conditions (Relative humidity of 100% and temperature of 25 ± 2 °C) ranged from about 3 months to 7 years

– indicating huge variation in the quality of various galvanic anodes. The analysis of the physico-chemical characteristics of the encapsulating mortar of pristine and aged galvanic anodes showed that the average SL_{min} depends on the pH, activator content, total pore volume, and critical pore entry diameter of the encapsulating mortar and is irrespective of the mass of zinc. Also, the failure mechanisms of galvanic anodes observed during the GAP test are conceptualized and correlated to the properties of encapsulating mortar. Finally, a set of prescriptive and performance specifications for the selection of galvanic anode systems to achieve a target service life of repair is presented.

Keywords Corrosion · Reinforced concrete · Cathodic protection · Galvanic anodes · Guaranteed minimum service life

Abbreviations

%bwob	% By weight of binder
CP	Cathodic protection
EDS	Energy Dispersive Spectroscopy
GA	Galvanic anode
GAP	Galvanic Anode Performance
MIP	Mercury Intrusion Porosimetry
OCP	Open circuit potential

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RC	Reinforced concrete
SCE	Saturated calomel reference electrode
List of symbols	
SL_{\min}	Guaranteed minimum service life
m	Mass loss of zinc (grams)
I	Corrosion current (Ampere)
t	Time (seconds)
M	Molar mass of zinc (65.382 g/mol)
z	Valency of zinc (2)

1 Introduction

Corrosion of steel is one of the major durability concerns, reducing the service life of reinforced concrete (RC) structures [1]. According to the NACE Impact Report 2016, the cost associated with the corrosion and repair of RC structures accounts for about 4 to 5% of the global GDP and around 50% of RC structures hit repair within 10 years from the time of construction [2]. The conventional approach of patch repair fails to address the root cause of the corrosion, resulting in premature failure of repairs (say, within every five years), repeated repairs and increased life cycle cost [3]. Premature failure of repairs and repeated repairs can result in a huge wastage of steel and concrete, affecting the sustainability of the built environment [4]. Cathodic protection (CP) using galvanic anode (GA) is one of the proven electrochemical techniques to prevent/control the corrosion of steel in concrete [5–8]. These systems can be designed to effectively control corrosion for up to 25 years, followed by the replacement of GAs [7]. In recent years, the technology has gained widespread acceptance. For instance, in India, the repair of RC structures using GAs has increased by 100 times from 2010 to 2020 [3]. However, huge variations have been observed in the properties of various GAs available in the concrete repair market, the quality of installation, and their resulting performance. Hence, there is a possibility of defaming of this technology, which otherwise could be of immensely useful to extend the service life of the huge inventory of concrete structures. This paper presents the performance of five commercially available GAs assessed using an earlier

developed short-term accelerated test method (known as the Galvanic Anode Performance [GAP] test). In addition, a methodology to estimate the guaranteed minimum service life (SL_{\min}) of GAs in concrete systems exposed to specific environmental conditions is presented, which can be used as a tool for the selection of durable GAs to extend the service life of concrete structures.

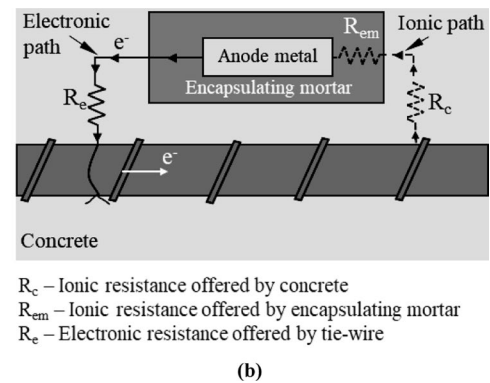
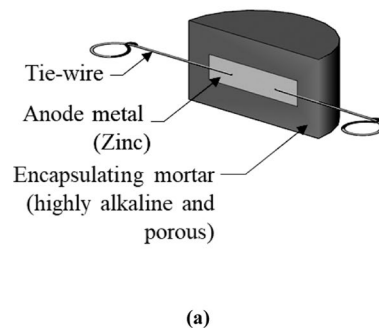
The remaining paper is arranged as follows: First, a review of the factors influencing the performance of GAs in concrete systems is presented. Next, the physico-chemical characteristics of five commercially available pristine GAs are presented. Following that, the performance of these GAs assessed using the GAP test is discussed. After that, a methodology to estimate the SL_{\min} of GAs in specific exposure conditions is presented. Next, the failure mechanism of GAs in the GAP test is discussed. Finally, a set of prescriptive and performance specifications for the selection of GAs is presented.

1.1 Factors influencing the performance of galvanic anodes

The mechanism of CP involves the polarization of the metal to be protected towards the cathodic regime by the supply of electrons from a current source (called impressed current cathodic protection) or a highly electronegative metal (called galvanic cathodic protection) [9]. This paper presents the research work on the latter, and the former will not be discussed herein. Figure 1a shows the schematic of the cross-section of a typical discrete GA. A typical discrete GA consists of a highly electronegative metal embedded inside a specially formulated cementitious encapsulating mortar. The anode metal has tie-wires attached to it, which are used to connect to the metal that has to be protected (i.e.) steel reinforcement. Figure 1b shows the schematic of the mechanism of CP using a GA, represented with the help of resistors for easy understanding. The mechanism involves the transfer of electrons (electronic conduction) through the tie-wires and the transfer of ions (ionic conduction) through the encapsulating mortar and concrete [5]. Hence, the resistivity of the encapsulating mortar and concrete plays a predominant role in the performance of GAs [9, 10]. Typically, the resistivity of concrete is in the range of 10 to 300 k Ω .cm, which is very high to that of mud or soil (up to 1 k Ω .cm) [11, 12]. The



Fig. 1 Schematic showing **a** Cross-section of a typical galvanic anode and **b** Principle of cathodic protection in concrete



resistivity of the encapsulating mortar depends on the chemical additives (say, activators and humectants) added to enhance the performance of GAs and is discussed later in this section. The factors influencing the performance of GAs in concrete systems are discussed next.

The performance of GAs depends on the properties of the anode metal, encapsulating mortar, and tie-wires [13]. Typically, anode metals are made of magnesium, aluminium, zinc, or their alloys [14]. Zinc is widely used for application in concrete structures because of its high electrochemical efficiency [15]. However, the efficiency of zinc depends on the microclimate surrounding it, such as pH, relative humidity, ionic conductivity, and pore-size distribution, which can be achieved by incorporating activators and humectants in the encapsulating mortar [15–17]. Activators (alkali- and halide-based) can help maintain a continued corrosive environment and increase the dissolution kinetics of zinc [18]. Alkali activators such as LiOH, NaOH, and KOH can provide a high pH (pH of 14+) environment and can enable the active corrosion of zinc [19]. Halide activators such as F, Cl, Br, and I can act as catalysts to aid the continued corrosion of zinc [20]. Humectants such as LiBr, LiNO₃, and CaCl₂ are hygroscopic materials which can help maintain the desired relative humidity in the encapsulating mortar and at the zinc-encapsulating mortar interface to facilitate the ionic conductivity and corrosion of zinc, respectively [21]. Another important aspect is the pore-size distribution of the encapsulating mortar. The encapsulating mortar should be porous and well-interconnected to accommodate the zinc oxidation products and facilitate the two-way transport of ions and oxidation products [22]. In addition, external factors such as the

relative humidity, temperature, and time of wetness of the service exposure will influence the performance of GAs [16, 23]. Also, the performance of the GAs depends on other factors, such as the location, size, orientation of the anodes, the steel density, the level of chlorides, and the resistivity of concrete [16]. In general, the long-term performance of GAs is influenced by the synergistic effects of all these parameters. Failure to comply with the desired properties of the encapsulating mortar could result in the passivation or failure of GAs, which is discussed next.

Zinc passivates to form zinc oxide or hydroxide, which can occupy 2.34 times more volume than zinc [22]. The formation of the oxide layer can affect the long-term performance of GAs [7, 13]. Also, the oxidation products diffusing/migrating away from the zinc can clog the pores and hinder the ion transport in the encapsulating mortar [13]. These factors can result in premature failure within 1/3rd to 1/4th of the theoretical consumption limit of GAs [21].

2 Research significance

In this paper, a methodology to estimate the guaranteed minimum service life of GAs in concrete systems exposed to specific environmental conditions is presented, which can be used as a tool for the screening of GAs. The findings in this paper show that the performance of GAs depends on the physico-chemical characteristics (pH, activator content, total pore volume, and critical pore entry diameter) of the encapsulating mortar and is irrespective of the mass of zinc. This would urge the GA manufacturers to improve the quality of the encapsulating mortar and develop more durable GAs. A set of prescriptive and performance

specifications was developed which can help design durable GA systems. These specifications will be crucial for repair engineers and decision-makers to develop repair strategies using GAs that will guarantee a target service life of the repair.

3 Experimental methods and materials

Commercially available GAs from five manufacturers were used in this study and are designated as Anodes A, B, C, D and E. These GAs have varying encapsulating mortar, anode metal, and tie-wire properties, which were determined using physico-chemical and electrochemical characterization studies and are presented in this section. Then, the details of the experimental programs to assess the performance and estimate the SL_{min} of GAs are presented.

3.1 Characteristics of galvanic anodes

The chemical composition of the anode metal, tie-wire and encapsulating mortar was determined using Energy Dispersive Spectroscopy (EDS) analysis. For the other physico-chemical properties of pristine and aged GAs, chunks of encapsulating mortar near the zinc (1 to 2 mm) were extracted and studied. The nominal pH of the encapsulating mortar samples was determined using a pH electrode. All the GAs used in this study are alkali-activated as per the manufacturer's product specification. Lithium is commonly used as the activating chemical for alkali-activated GAs and has been reported well in the literature [5–10].

Hence, lithium (in the form of LiOH) was assumed as the activating chemical for all the GAs used in this study. The amount of LiOH was calculated by conducting acid–base titrations on the encapsulating mortar samples. A titration curve between the amount of acid added and the nominal pH of the solution was generated. The amount of acid required to neutralize the hydroxyl buffer in the encapsulating mortar was calculated from the inflection point of the acid–base titration curves. This value was used to calculate the approximate amount of LiOH in the mortar samples. The nominal pH is not a true pH as most pH meters are not able to read accurately at very high pH values in excess of 14. Hence, the actual pH can be calculated based on the amount of LiOH present in the encapsulating mortar. The procedure to calculate the amount of LiOH and the pH buffer capacity (or calculated pH) is available in the literature [13]. The pore volume and critical pore diameter of the encapsulating mortar were determined using the Mercury Intrusion Porosimetry instrument. The details of the sample preparation, test procedures and calculations for determining all properties mentioned above are available elsewhere [13]. Then, the performance of GAs was estimated using the GAP test and is presented next.

3.2 Galvanic anode performance test

Galvanic Anode Performance (GAP) test is a short-term accelerated test that simulates the process of CP of steel in concrete systems. The details of the development of the GAP test are available

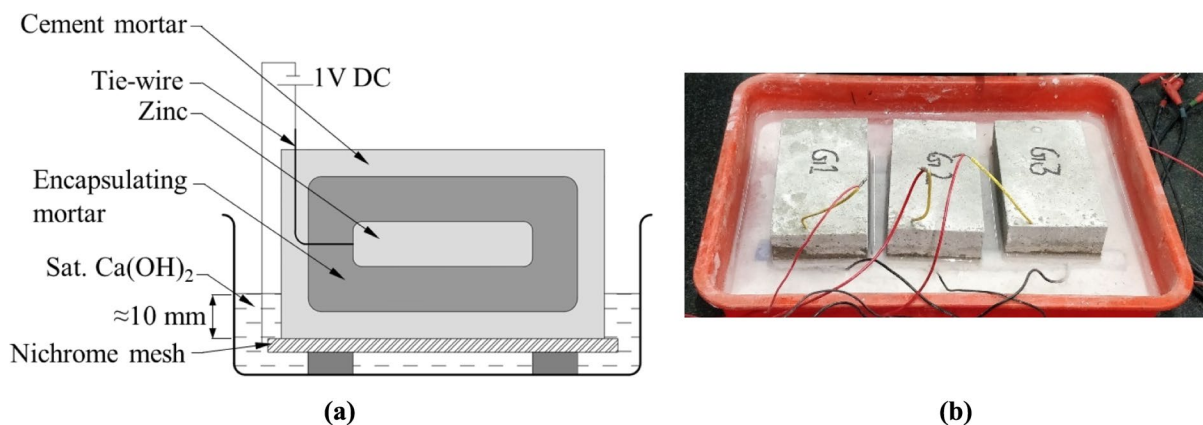


Fig. 2 Galvanic anode performance test **a** Schematic and **b** Photo



elsewhere [24]. Figure 2 shows the schematic and photo of the GAP test. The GA was embedded in a cement mortar made with a w/c ratio of 0.5, and the unit was called the GAP specimen. Ordinary Portland Cement (OPC) conforming to IS 269 and fine aggregate consisting of 50–50 mix of sands of grade II and III conforming to IS 650 were used to cast the GAP specimens [25, 26]. The GAP specimens were cast in such a way that a cover of ≈ 10 mm was provided on all sides. Saturated calcium hydroxide [$\text{Ca}(\text{OH})_2$] solution with a pH of ≈ 12.5 was used as the electrolyte for the testing. The electrolyte was refilled at regular intervals such that the solution level was maintained at ≈ 10 mm from the base of the GAP specimen at all times. Nichrome (Nickel–Chromium) mesh with a surface area five times larger than the surface area of the anode metal was taken as the counter electrode. The GAP specimen was connected to the positive terminal, and the nichrome mesh was connected to the negative terminal of a DC power source. A potential difference of 1 V was applied between the terminals, and the output current from the GAP specimen was measured regularly till failure (output current $< 0.1 \mu\text{A}$). The electrochemical capacity (total electrical charge drawn) by the GA was determined by integrating the area under the output current vs. time curve, and from which the SL_{\min} was estimated. To estimate SL_{\min} , the corrosion rate of zinc (corrosion current) is required and is determined through potentiostatic polarization scan (PSS) and is presented next.

3.3 Estimation of guaranteed minimum service life of galvanic anodes

The input parameters needed to estimate SL_{\min} are the (i) electrochemical capacity (total electrical charge drawn) of GA, which can be determined using the GAP test presented in the *Galvanic anode performance test* section, and (ii) corrosion current of GA. The corrosion current of a GA represents the rate at which it will be consumed when connected to another more electropositive metal (say, steel). The corrosion current of GAs was determined using PSS. PSS involves polarising a metal from its open circuit potential (OCP) to a different potential and holding that potential constant until a steady state current is reached. Overpotential represents the shift in the OCP of a metal when connected to another metal. In other words, when a cell is producing a current, the electrode potential changes from its zero-current value, E , to a new value E' . The difference between E and E' is called the electrode's overpotential. It has to be noted that the overpotential is different from the mixed potential of the system. In general, overpotential represents the difference in the OCP of the GA before and after connection to steel.

The overpotential of GAs was determined by conducting an OCP test, as shown in Fig. 3(a). The test setup consists of casting GAP specimens, as described in the *Galvanic anode performance test* section. Then, the GA was connected to a severely corroding steel rebar using a switch arrangement. The OCP of the steel rebar was $-400 \text{ mV}_{\text{SCE}}$. A saturated

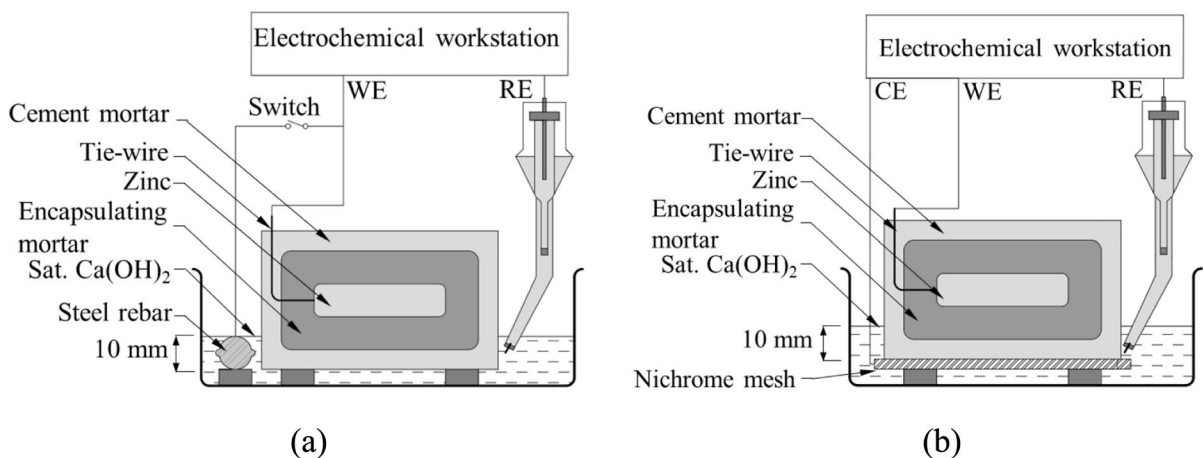


Fig. 3 Schematic of the test setups used to determine **a** overpotential and **b** corrosion current of galvanic anodes

calomel electrode (SCE) was used as the reference electrode and was positioned near the GA and away from the steel rebar. It has to be highlighted that positioning the reference electrode away from the steel and near the GA is very important to measure only the OCP of the GA and not the potential of the combined system (steel and GA). Initially, the switch was kept in the OFF condition, and the OCP measurement was started. The potentiostat started recording the OCP of the GA alone and was represented as E. Once the OCP of the GA was stabilized (say, after 120 s), the switch was turned ON. At this point, a sudden jump in the OCP was observed, and the measured potential was represented as E'. The difference between E and E' gives the overpotential of the GA. The overpotential was used as the static potential in the PSS to measure the corrosion current and is explained next.

A three-electrode test setup, as shown in Fig. 3b, was used to obtain the PSS of the GA, from which the corrosion current of the GA was determined. The GAP specimen was the working electrode, the nichrome mesh was the counter electrode, and SCE was the reference electrode. The GAs were polarized in the anodic direction to fixed static potentials (measured overpotentials) until a steady state current was achieved.

4 Results and discussions

4.1 Characteristics of pristine galvanic anodes

Table 1 presents the characteristics of the five GAs used in this study. Anodes A, B, C, D and E have different zinc masses, surface areas, and properties of the encapsulating mortar and tie-wires. The elemental composition of the anode metal indicates that Anodes A and B were made of 100% zinc, whereas Anodes C, D and E were made of 95, 98 and 90% zinc, respectively. It can be inferred that the metals of Anodes A and B were made of pure zinc (100% zinc), whereas Anodes C, D and E were made of zinc with some alloying additions. The iron composition in all anodes was less than 0.001% – conforming to Type II GA specification as per ASTM B418 [27]. Type II GAs are specified to be made of high-grade zinc with an iron content of less than 0.001%. Such a reduced iron content would prevent the intergranular corrosion of the anode metal at temperatures higher than

Table 1 Characteristics of pristine galvanic anodes

Characteristic	Anodes				
	A	B	C	D	E
Zinc (%)	100	100	95	98	90
Zinc mass (g)	55	110	75	60	60
Zinc surface area (cm ²)	≈ 40	≈ 30	≈ 30	≈ 30	≈ 40
Nominal pH	≈12.9	≈10	≈12.7	≈10	≈10
W _{LiOH} (% bwob)	≈14	0	≈ 45	0	0
Calculated pH	≈14	≈10	≈14	≈10	≈10
Pore volume (mm ³ /g)	200	115	370	52	192
Critical pore size (μm)	4.8	3.5	0.5	2.3	1.5

50 °C. The mass of zinc in Anodes A, B, C, D and E was 55 g, 110 g, 75 g, 60 g and 60 g, respectively. For an aqueous environment, the mass of zinc is one of the critical parameters that determines the service life of GAs. However, in cementitious systems, the consumption of the entire zinc may not occur due to the unavailability of a continued corrosive environment for the zinc, which is discussed later in this section. In another long-term monitoring study by the authors, it was found that only 1/4th of the mass of zinc of the GA had been consumed after 12 years of exposure to a near-coastal environment [13]. It was also observed that the oxides of zinc stopped diffusing/migrating away from the zinc, formed an insoluble barrier around the zinc and obstructed the ionic movement for the corrosion to occur. Hence, the mass of zinc may not be a critical parameter for the performance of GAs for concrete systems. The surface area of zinc in Anodes A, B, C, D and E was 40 cm², 30 cm², 30 cm², 30 cm² and 40 cm², respectively. The surface area of the zinc has a direct impact on the output current supplied by GAs. The higher the surface area of zinc, the higher the possibility for the formation of anodic sites and the higher the supply of electrons. The surface area of zinc in Anodes A and E is higher than all the other anodes. However, apart from the availability of high surface area, the corrosion of zinc depends on the micro-climate around it and is discussed next.

The micro-climate around the zinc depends on the physico-chemical properties of the encapsulating mortar, such as the pH, activator content and the pore size distribution (pore volume and critical pore size). Table 2 presents the chemical composition of the encapsulating mortar of all anodes. It can be observed



Table 2 Chemical composition of the encapsulating mortar and tie-wire of pristine galvanic anodes

Element	% wt.									
	Encapsulating mortar					Tie-wire				
	A	B	C	D	E	A	B	C	D	E
Magnesium	0.2	1.0	0.7	0.6	–	–	–	–	–	0.29
Aluminium	6.3	2.2	0.9	1.8	4.2	–	–	–	–	–
Silicon	2.3	5.1	0.5	7.2	5.4	–	–	–	–	–
Calcium	12.5	18.1	17.2	35.2	21.2	–	–	–	–	–
Potassium	0.3	–	–	5.5	0.1	–	–	–	–	0.24
Sodium	–	–	1.2	0.8	1.0	–	–	–	–	–
Iron	0.3	4.1	–	–	0.4	53.2	51.9	56.7	76.5	89.0
Carbon	4.2	8.6	16.2	5.9	7.8	4.2	9.8	5.9	8.8	7.1
Oxygen	50.6	38.3	63.0	42.6	52.7	–	21.3	–	14.6	1.8
Zinc	1.7	–	–	–	0.6	–	16.8	–	–	1.0
Titanium	–	0.5	–	–	–	–	–	–	–	–
Chromium	–	–	–	–	–	37.1	–	37.3	–	–
Sulphur	–	–	–	–	5.0	–	–	–	–	0.2
Neon	–	–	–	–	–	5.3	–	–	–	–
Chloride	–	–	–	–	0.2	–	–	–	–	–
Remaining	21.6	22.1	0.3	0.4	1.4	0.2	0.2	0.1	0.1	0.37
Lithium	Could not be detected in EDX									

that Calcium was present in the encapsulating mortar of all GAs and might be from the calcium oxide present in the cementitious encapsulating mortar. In addition, traces of alkali, such as potassium, were present in Anode A and sodium in Anodes A, C, D and E. The presence of Lithium could not be observed in the EDS analysis because of its low atomic number (atomic number 3). In general, elements with atomic numbers less than Carbon could not be detected in EDS.

The nominal pH of the encapsulating mortar of Anodes A, B, C, D and E was ≈ 12.9 , ≈ 10 , ≈ 12.7 , ≈ 10 and ≈ 10 , respectively. The activator content (expressed as a percentage of LiOH content) of encapsulating mortars of Anodes A, B, C, D and E was ≈ 14 , 0, ≈ 45 , 0 and 0% bwob, respectively. The activators will enhance the pH buffer capacity of the encapsulating mortar. The calculated pH of Anodes A, B, C, D and E was ≈ 14 , ≈ 10 , ≈ 14 , ≈ 10 , and ≈ 10 , respectively. The corrosion rate of zinc will be high when the pH of the surrounding electrolyte is more than 12.5, whereas the zinc will tend to passivate when the pH drops below 12 [20–22]. Anodes A and C have a suitable environment (high pH and pH buffer capacity) to achieve a continued corrosive

environment for zinc. On the contrary, Anodes B, D and E have a low-pH environment (pH of ≈ 10) at the zinc-encapsulating mortar interface that may not favour the corrosion of zinc. In addition to pH, the pore size distribution of the encapsulating mortar will govern the transport process of the activating chemicals and the zinc oxidation products to maintain a corrosive environment for the zinc, which is explained next.

The encapsulating mortars should be designed in such a way that their pore size distribution should favour the diffusion/migration and accommodation of the zinc corrosion products and expose the fresh zinc metal for continued corrosion. The total pore volume (mm^3/g) of the encapsulating mortars of Anodes A, B, C, D, and E was 200, 115, 370, 52, and 92, respectively. The critical pore diameter (μm) of the encapsulating mortars of Anodes A, B, C, D, and E was determined as 4.8, 3.5, 0.5, 2.3, and 1.5, respectively. Anode A has a well-defined porous system with large diameter interconnected pores, sufficient to allow the movement of the activators and zinc oxide products. Anodes B, D and E have low pore volumes with small diameter interconnected pores. Anode C has a high pore volume to accommodate the oxidation products;

however, it has a small diameter interconnected pore system that may block the movement of the corrosion products.

In addition, the material of tie-wire can also affect the long-term performance of GAs. For example, mild steel tie-wires can undergo surface corrosion during the transportation and storage of GAs. Also, the rust layer on tie-wires of the GAs may hinder the supply of electrons to the steel rebars as expected. Table 2 presents the chemical composition of the tie-wire of GAs. The tie-wires of Anodes A and C consist of a Chromium content of $\sim 37\%$, indicating the material is stainless steel, which can help prevent the corrosion of tie-wires during transportation, storage and at construction sites. However, the tie-wires of Anodes B, D and E are mild steel, which may undergo surface corrosion during transportation or storage. The overall performance of a GA depends on the synergistic performance of all components mentioned above. The performance of anodes assessed using the GAP test is presented next.

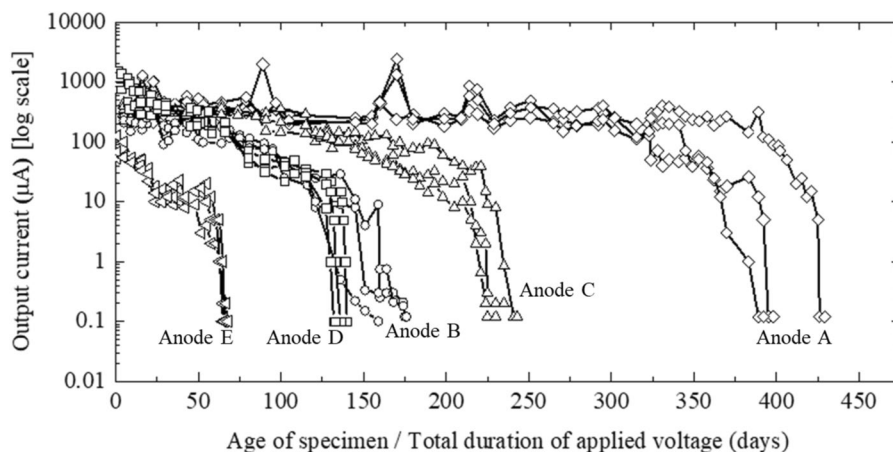
4.2 Assessment of performance of galvanic anodes

Figure 4 shows the output current supplied by GAs in the GAP test. It can be observed that all GAs supplied relatively high output currents at the beginning of the testing. After that, stable output currents were observed, followed by a gradual decay and a sudden drop. The experiment was terminated once the measured output current dropped to a value less than $0.1 \mu\text{A}$ and was defined as the failure of anodes. The area under each curve represents the electrochemical capacity or the total electrical charge transferred by

GAs. The performance of GAs can be assessed from two parameters, namely (i) instantaneous output current and (ii) total electrical charge. The capacity of a GA to supply a high instantaneous output current indicates its ability to supply more electrons to suppress/control corrosion immediately after connecting it to corroding metal. In other words, the instantaneous output current can be used as a qualitative parameter to choose/design GA systems suitable for either corrosion prevention (cathodic prevention) or corrosion control (cathodic protection) situations. In a cathodic prevention case, there may not be a need for the supply of high instantaneous output current due to negligible ongoing corrosion. However, in a cathodic protection case, the GAs should supply high instantaneous output currents to suppress the ongoing corrosion. The individual and instantaneous output currents measured from Anode A during the first 100 days were more than $350 \mu\text{A}$, whereas Anodes B, C, and D supplied more than $150 \mu\text{A}$. Anode E failed within 60 days of testing. From this, it can be inferred that Anode A might be suitable for conditions where the ongoing rate of corrosion is high (Cathodic protection case), provided it can supply an adequate charge in the GAP test, which will be explained next. The ability of Anode A to supply high initial output currents could be due to the high surface area of zinc (40 cm^2) compared to Anodes B, C, and D, all with a surface area of 30 cm^2 .

Secondly, the total charge supplied by GAs was calculated by integrating the output current versus the time plot. The total charge supplied by GAs represents their electrochemical capacity – a parameter that determines the service life of GAs. In general,

Fig. 4 Output current supplied by galvanic anodes in the GAP test



the electrochemical capacity of GAs depends on the mass of the zinc. However, in cementitious systems, the electrochemical capacity of GAs depends on the micro-climate at the zinc-encapsulating mortar interface, which governs the reaction kinetics. Anode A failed at around 420 days of testing, whereas Anodes B, C, D and E failed at around 160, 230, 130 and 60 days, respectively. At the end of the GAP test, Anode A exhibited better performance, and Anode E showed poor performance. However, it may not always be convenient to assess the performance of GAs based on the total charge supplied; hence, a parameter termed the guaranteed minimum service life was developed, and the same was estimated using Faraday's law and is presented next.

4.3 Estimation of guaranteed minimum service life of galvanic anodes

The guaranteed minimum service life (SL_{\min}) represents a guaranteed time for a GA to perform in a specific exposure condition. The SL_{\min} of GAs was estimated using Faraday's law of electrolysis. The input parameters involved in estimating SL_{\min} are (1) total electrical charge transferred by GAs in the GAP test and (2) corrosion current (I) of GAs determined from PSS. The steps involved in estimating SL_{\min} are as follows: Step 1: Estimate the theoretical mass loss (m) of the anode metal as per Eq. (1) using the total electrical charge supplied by the GA in the GAP test, and Step 2: Estimate the SL_{\min} of the GA as per Eq. (2) using the theoretical mass loss (m) calculated from Step 1, and corrosion current (I) determined from potentiostatic scans.

$$m = \frac{Q \times M}{F \times z} \quad (1)$$

$$SL_{\min} = \frac{m \times F \times z}{I \times M} \quad (2)$$

where, Q is the electrical charge supplied (Coulomb), M is the molar mass of zinc (grams/mole), F is the Faraday's constant (96,485 Coulomb/mole), m is the theoretical mass loss (grams), I is the corrosion current (Ampere), z is the valency of the ions.

Figure 5 shows the variation in the OCP of GAs before and after connecting them to a steel rebar. The inset of Fig. 5 shows the zoomed-in region

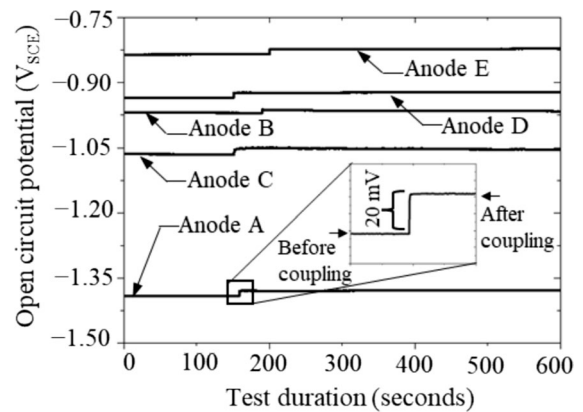


Fig. 5 Variation in the OCP of galvanic anodes before and after coupling with a steel bar

illustrating the jump in the OCP of Anode A when connected to the steel rebar. It can be observed that the OCP of Anode A before coupling (termed as E) was $-1390 \text{ mV}_{\text{SCE}}$ and after coupling (termed as E') was $-1370 \text{ mV}_{\text{SCE}}$. The difference between E and E' represents the overpotential and was determined as 20 mV. Similarly, the overpotential of Anodes B, C, D and E was 20, 25, 20 and 20 mV, respectively. It is important to highlight that the recorded overpotential is not the mixed potential in this case because the reference electrode was not placed in-between the GA and the steel; instead, it was placed away from the steel and touching the GA as detailed in the *Estimation of minimum service life of galvanic anodes* section. The determined overpotentials were used as the input parameter (as static potential) to determine the corrosion current. In other words, the GAs were anodically polarized to these overpotentials, and the resulting corrosion current density was measured and presented next. Figure 6 shows the evolution of the corrosion current density of GAs upon anodic polarization. It can be observed that current densities were high in the beginning and started to stabilize slowly. A steady-state current density value was chosen for the analysis. Steady-state was defined as the region when the slope of the curve between any two points (say, T and T+60 s) shall be less than $8 \text{ pA/cm}^2/\text{s}$. This slope was chosen based on a trial-end error method of selecting values and assessing their effect on the estimated SL_{\min} . The current densities of Anodes A, B, C, D and E were 1.2, 1, 0.8, 1.1 and $0.9 \text{ }\mu\text{A/cm}^2$, respectively, from which the corrosion

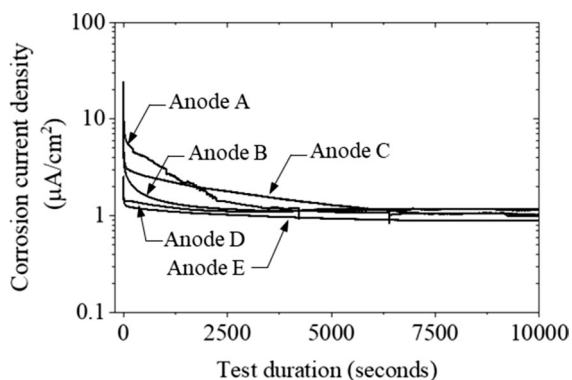


Fig. 6 Evolution of corrosion current density of galvanic anodes in potentiostatic scans

current (I) was calculated by multiplying them with the surface area of the anode metal. It has to be noted that the current densities recommended for designing cathodic prevention and cathodic protection systems are 0.02–0.2 and 0.2–2 $\mu\text{A}/\text{cm}^2$, respectively [5].

Figure 7 shows the estimated SL_{\min} for severe laboratory conditions (relative humidity of 100% and temperature of 25 ± 2 °C). It is assumed in the analysis that the corrosion rate (corrosion current) of zinc is constant throughout the year. The average SL_{\min} of Anodes A, B, C, D and E are 7, 2, 3, 2.5 and 0.2 years, respectively. It can be inferred that Anode A can perform for a guaranteed duration of seven years in a severe environment (relative humidity of 100%), whereas Anode E can perform only for around three months. This methodology can be used as a tool to assess the performance of GAs for different exposure conditions. In general, Anode A exhibited better performance than all the other anodes. The reasoning

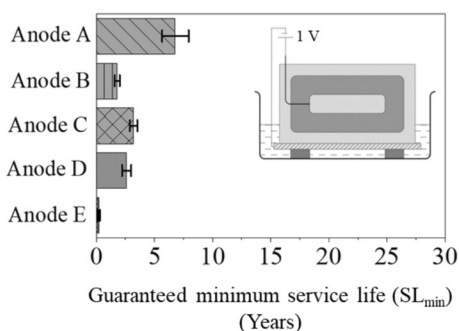


Fig. 7 Guaranteed minimum service life (SL_{\min}) of galvanic anodes in laboratory conditions

for the performance of GAs and their failure mechanisms are presented next.

4.4 Failure mechanisms of galvanic anodes

To understand the failure mechanisms of GAs, the failed GAP specimens were autopsied, and the physico-chemical characteristics of the encapsulating mortar of the failed GAs were determined and compared with that of the pristine GAs. For this, encapsulating mortar samples (chunks) were collected from the region close (1 to 2 mm) to the zinc core of the failed GAs. The objective of collecting samples close to the zinc core is to assess the condition of the micro-climate surrounding the zinc core. The failure mechanism of GAs could be due to (i) the unavailability of a high pH environment, (ii) the unavailability of a pathway for the movement of ions, or (iii) a combination of both mechanisms. Initially, the mortar chunks of the failed anodes were tested for their nominal pH using a pH electrode. Figure 8 compares the pH of pristine and aged GAs. It can be observed that there is no significant change in the pH (pH of 10) of Anodes B, D and E before and after failure. Hence, it can be concluded that the primary failure mechanism of Anodes B, D and E could be the unavailability of a high pH environment for the zinc to corrode. On the contrary, the pH dropped from 12.9–10 and 12.7–11 for Anodes A and C, respectively. Hence, the failure mechanism of Anodes A and C might not be only due to the low pH environment. To understand the failure mechanisms of Anodes A and C, the pore

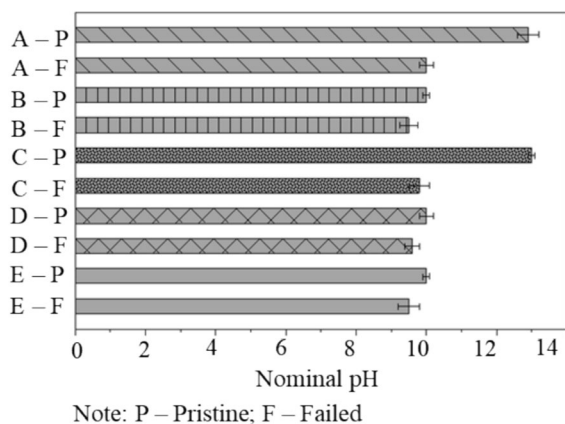
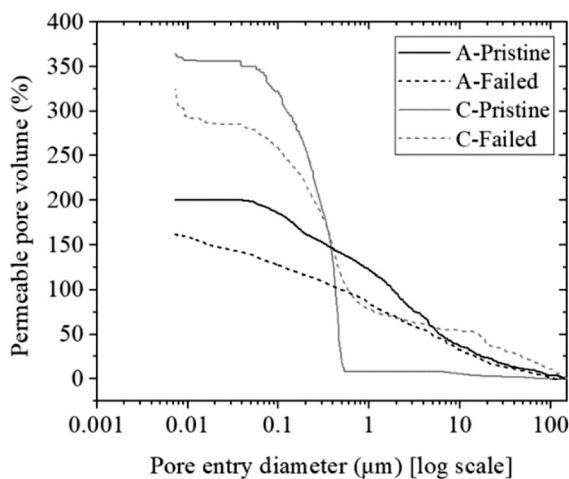


Fig. 8 Comparison of the pH of the encapsulating mortar of pristine and failed galvanic anodes

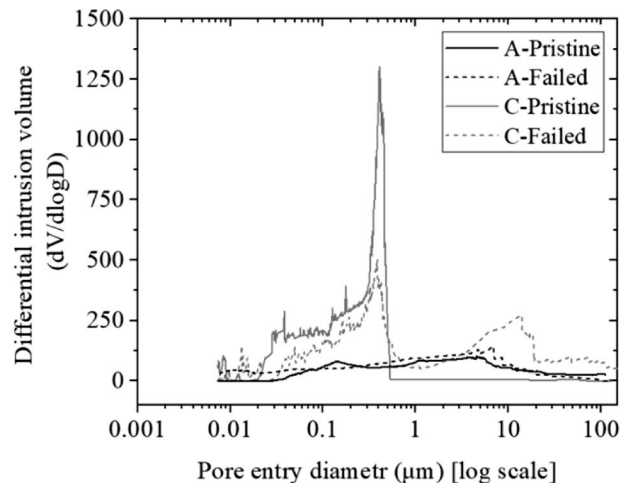


size distribution of the pristine and aged GAs was compared. Figures 9a and b show the data from mercury intrusion porosimetry of pristine and failed GAs. Figure 10 compares the total pore volume and critical pore diameter of the pristine and aged GAs. The analysis showed that pore volume (mm^3/g) reduced from 200 to 180 and 370–320 for Anodes A and C, respectively. The critical pore diameter (μm) has reduced from 0.5 to 0.4 for Anode C. For Anode A, the critical pore diameter (μm) has increased from 4.8 to 6, which might be due to the formation of cracks in the encapsulating mortar due to the expansive pressure offered by the zinc oxidation products. The critical pore size is the most probable pore size of any porous system. The increase in the critical pore size of Anode A might have helped the diffusion of the corrosion products away from the zinc, favouring the enhanced performance of Anode A. It can be assumed that the failure mechanism of Anodes A and C could be a combination of the reduction in the pH and the reduction in the pore volume of the encapsulating mortar.

In general, the pH of the encapsulating mortar has decreased for all the GAs, causing a low pH environment that does not favour the continued corrosion of zinc. The total pore volume has decreased for Anodes A and C, which might have blocked the pores, reduced the ionic conductivity, and led to the failure of GAs. The proposed failure mechanism of GAs in



(a)



(b)

Fig. 9 Data from mercury intrusion porosimetry of pristine and failed galvanic anodes; **a** cumulative pore volume plot and **b** differential intrusion volume plot

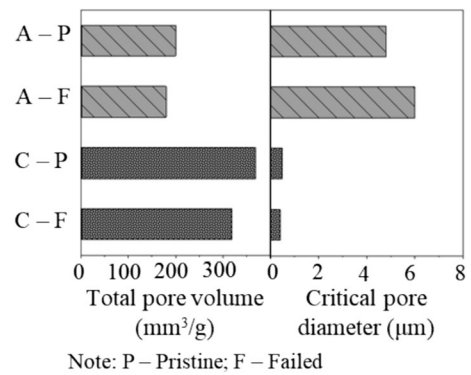


Fig. 10 Comparison of the total pore volume and critical pore diameter of the encapsulating mortar of pristine and failed galvanic anodes

the GAP test is illustrated in Fig. 11. In general, the oxides of zinc stopped diffusing/migrating away from the zinc, formed an insoluble barrier around the zinc and obstructed the ionic movement, and caused the failure of GAs.

5 Specifications for galvanic anodes

Table 3 presents a set of prescriptive and performance specifications for the selection of GAs, which are explained below:

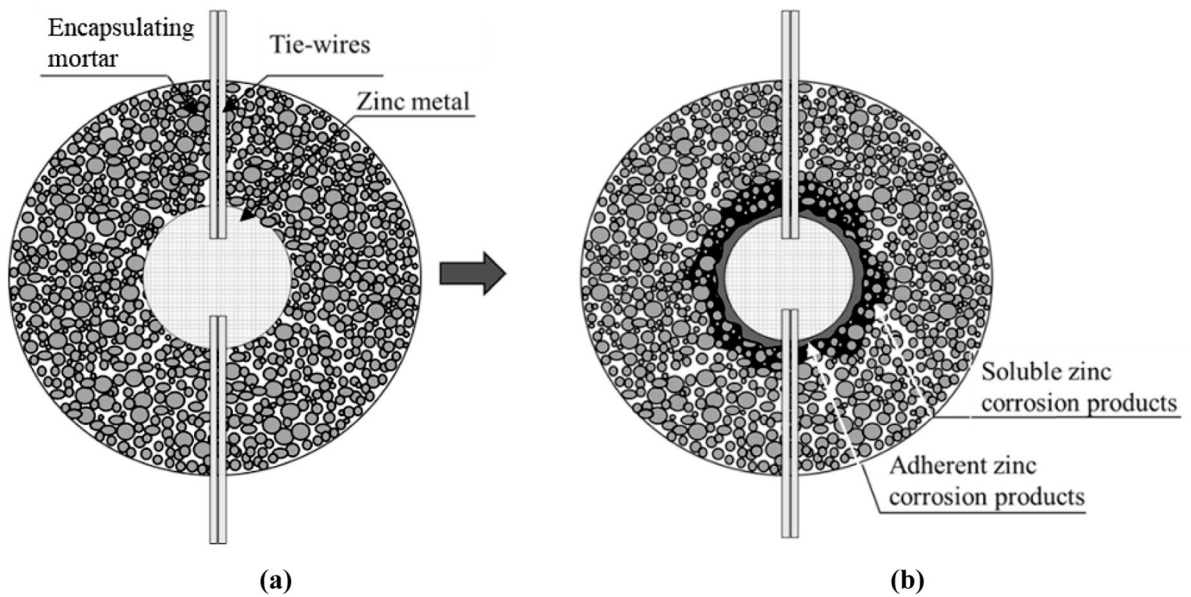


Fig. 11 Schematic showing the conceptualized failure mechanism of galvanic anodes in the GAP test **a** Pristine galvanic anode and **b** Failed galvanic anode

Table 3 Specifications for galvanic anodes for concrete applications

No	Parameter	Specifications
1	Zinc composition of the galvanic metal (as per ASTM B416 -16a)	90–100%
1	Open circuit potential of the anode metal (without removing the encapsulating mortar) after immersion in water for 15 min	< -1000 mV versus Cu/CuSO ₄ electrode
2	Calculated pH of the alkali-activated encapsulating mortar surrounding the anode metal until the target service life	> 13.6
3	Porosity of encapsulating mortar for anodes intended to be used in atmospherically exposed concrete elements (measured as per ASTM D4404-10) [28]. This point is not applicable for anodes intended to be used in submerged conditions	$> 20\%$
4	Material of tie-wire	Stainless steel or corrosion-resistant metal
5	Distance between the tie-wires, where they protrude out of the anode metal	> 0.5 mm
6	Connection between anode metal and tie-wire(s)	Tie-wires must be die-cast into the anode metal <i>Note: Screw connection or welded connections are not allowed</i>
7	GAP Test – All individual and instantaneous output current measured from the GA during the first 100 days of the GAP test with an applied potential difference of 1 Volt	> 200 μ A
8	GAP Test – Cumulative electrical charge passed (i.e., area under the Output Current Vs Time of Applied Potential Difference curve) during the first 100 days of GAP test with an applied potential difference of 1 Volt	> 3000 Coulomb

- a) The chemical composition of the anode metal shall conform to the specifications given in ASTM B418-16a with a high-grade zinc content ranging from 90 to 100% [27]. The iron content in the galvanic metal shall be less than 0.001% to prevent intergranular corrosion at temperatures higher than 50 °C.
- b) The open circuit potential (OCP) of the GA (without removing the encapsulating mortar) after immersion in water for 15 min shall be more electronegative than 1000 mV_{Cu/CuSO₄}. This criterion can help eliminate the use of GAs with passivated zinc. The OCP of a GA will tend to shift towards a more electropositive direction upon the passivation of the zinc. In addition, the immersion of GAs in water shall not be more than 15 min, which can result in the leaching of the activating chemicals from the encapsulating mortar.
- c) The calculated pH of the alkali-activated encapsulating mortar surrounding the anode metal shall be more than 13.6 and is expected to retain till the target service life.
- d) The pore volume of the encapsulating mortar of the GA shall be more than 20% to achieve sufficient porosity for the accommodation and transport of the zinc oxidation products and the two-way transport of the activating chemicals [13].
- e) The material of the tie-wire shall be stainless steel or other corrosion-resistant material to prevent surface corrosion during transportation and storage. The tie-wires shall be die-cast to the zinc core and not welded or screwed. The distance between the tie-wires shall be well-spaced to prevent tie-wire corrosion due to the accumulation of water and oxygen in the gap between the tie-wires [13].
- f) GAP Test – All individual and instantaneous output current measured from the GA during the first 100 days of the GAP test with an applied potential difference of 1 V shall be more than 200 µA.
- g) GAP test – The cumulative electrical charge passed (i.e., the area under the Output Current Vs Time of Applied Potential Difference curve) during the first 100 days of the GAP test with an applied potential difference of 1 V shall be more than 3000 Coulomb.

6 Summary and conclusions

Huge variations have been observed in the properties of GAs available in the concrete repair market and their resulting performance. This study presents the performance of five commercially available GAs assessed using an earlier developed short-term accelerated test method [known as the Galvanic Anode Performance (GAP) test]. The following are the major conclusions drawn:

- (1) The performance of GAs in the GAP test was assessed using (i) instantaneous output current and (ii) total electrical charge supplied. The individual and instantaneous output currents measured from Anode A during the first 100 days were more than 350 µA, whereas Anodes B, C, and D supplied more than 150 µA. Anode E failed within 60 days of testing. Secondly, Anode A failed at around 420 days of testing, whereas Anodes B, C, D and E failed at around 160, 230, 130 and 60 days, respectively. At the end of the GAP test, Anode A exhibited best performance and Anode E showed worst performance, among tested GAs.
- (2) A methodology to estimate the guaranteed minimum service life (SL_{min}) of GAs in concrete systems exposed to specific environmental conditions is presented. The SL_{min} represents a guaranteed time for a GA to perform in a specific exposure condition. The methodology involves the determination of the electrochemical capacity (total electrical charge drawn) of GAs from the GAP test and the corrosion rate of GAs from potentiostatic polarization scans. This methodology can be used as a tool to assess the performance of GAs for different exposure conditions.
- (3) The SL_{min} of Anodes A, B, C, D and E for laboratory conditions simulating severe exposure conditions (relative humidity is 100% and temperature is 25 ± 2 °C) is 7, 2, 3, 2.5 and 0.2 years, respectively. It can be inferred that Anode A can perform for a guaranteed duration of seven years in a severe environment, whereas Anode E can perform only for around three months.
- (4) Anode A showed better performance than Anodes B, C, D and E. The high surface area of the anode metal (40 cm²), high pH (≈12.9) and large pore volume (200 mm³/g) of the encapsulating mortar

have enabled its better performance. The analysis of the physico-chemical characteristics of the encapsulating mortar of pristine and aged GAs showed that the performance depends on the pH, activator content, total pore volume, and critical pore entry diameter of the encapsulating mortar and is irrespective of the mass of the zinc.

- (5) A set of prescriptive and performance specifications for the selection of GAs for concrete systems is developed and presented. These specifications will be crucial for repair engineers and decision-makers to develop repair strategies using GAs that will guarantee a target service life of the repair.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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