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Performance Assessment of Specialist Conductive Paint for Cathodic Protection of Steel in Reinforced Concrete Structures

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Abstract

ICCP system provides effective corrosion protection in a chloride environment. This research evaluates the feasibility of zinc rich paints (ZRP) as ICCP anode for RC structures. The preliminary investigation showed the application of three layers of ZRP with medium concrete surface roughness and use of Cu/Nb/Pt wire as primary anode gives maximum bond strength and uniform current distribution across the ZRP coating. Moreover, polarization results showed satisfactory performance of the ZRP anode coating subjected to a current density of 12.5 mA/m^2. Anode was found to be vapour permeable and effectively provide protection with a service life up to 15 years.

Keywords: Steel reinforced concrete; Conductive Paint; Microstructure, Coating Anode; Cathodic Protection; Service Life, Permeability, Polarization

1.0 Introduction

One of the major challenges of recent years in the construction industry has been to extend the service life of reinforced concrete structures, especially those exposed to the coastal environment [1]. The

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corrosion of steel reinforcement in concrete structures leads to rust formation, cracking, delamination and degradation of structure and is considered as the biggest factor for the damage in bridges and construction industries [2–4]. To deal with the issue many researchers have studied and developed various corrosion mitigation techniques which include conventional patch repair, corrosion inhibitors and electrochemical treatment. Electrochemical techniques such as cathodic protection, cathodic prevention, electrochemical realkalisation and electrochemical chloride extraction are proved as effective methods for corrosion prevention and mitigation [5–7]. Impressed Current Cathodic protection (ICCP) has proven to be the most effective approach for preventing and minimizing corrosion initiation in RC structures subjected to high chloride environment [8–12]. The principle of ICCP is to negatively shift the steel/concrete/electrode potential of the protected structure by delivering sufficient polarization current, such that initiation and propagation of corrosion are suppressed and corrosion failure will not occur during the lifetime of the structure, pitting is prevented and steel becomes passivated [9,13–15].

The most critical component of any cathodic protection is the design of an effective anode system to distribute protection current efficiently and economically to the structural elements to be protected. Also, it must be easy to install and possess long term durability. For ICCP of reinforced concrete, research has been centred on the development of anode materials, e.g. thermal sprayed zinc [16–24], titanium anodes [25,26], conductive coating [27–31], and conductive cementitious overlay anodes [9,32–35]. However, the researchers are still trying to find new anode materials with improved performance characteristics, such as higher bond strength, lower acidification, low cost and improved installation convenience [11].

Conductive coating anode systems include organic and mineral coating containing a variety of formulations of carbon pigmented solvent or water dispersed coatings and metallic coatings such as thermal sprayed zinc. Zinc based anodes are mostly preferred for their application in reinforced concrete [8,36]. However, its use is limited mainly as sacrificial anodes [37]. Generally, they are used

as part of patch repair system to enhance the longevity of the repairs with an estimated life time of around 10 years. Sergi and Whitmore [22] reported the performance of sacrificial zinc anodes in concrete after monitoring them for 10 years and they were successful in providing the required current. Sekar *et al.* [29] used zinc overlay as a sacrificial anode and observed that potential shift is considerable near the anode and decreases on increasing distance from the anode, implying non-uniform current distribution. Thus, the use of zinc as sacrificial anode cathodic protection (SACP) does not show a uniform distribution of current [29]. Moreover, it has been observed by many researchers that galvanic zinc is unable to deliver the required current unless it is periodically wetted [19,33,38,39]. However, its current delivery could be restored by either direct wetting the anode [38] or by using humectants [27,37,40–42]. Humectant solutions keep up the moisture level in the concrete thus reducing the electrical resistivity of concrete and anode concrete interface [40,42]. Hence, galvanic zinc anode systems without humectants should only be applied in the aggressive environment such as high humidity, soils or wet/dry condition, because only in these conditions they are able to fulfil required current demand to satisfy the 100 mV decay performance criterion [43].

Various forms of zinc (Zn) anodes have been developed such as thermally or arc sprayed coating of Zn, Zn-Al or Al-Zn-In and rolled zinc sheets. Thermally sprayed zinc (TSZ) anodes are found to be more effective to be used as an ICCP anode, however, can be used for both sacrificial and ICCP systems [34,37]. The main failure reason for thermal sprayed zinc as ICCP systems is the loss of bond between anode and concrete substrate or high voltage demand greater than operating limits [44]. During operation with SACP with TSZ anode, Dugarte and Sagues [45] observed oxidation products of Zn (white corrosion product) at Zn-cement interface leading to loss of bond [45]. For long term performance of TSZ anode, it is essential to maintain moisture at Zn-concrete interface. This lowers the voltage needed for the effective operation of ICCP systems, increases the performance of the sacrificial system, and redistribute anode dissolution products into the concrete pore structure [16]. Rolled Zinc Sheet and metallized Zn-Al is found unsuitable for ICCP as they lead to blistering and loss of adhesion [34,46]. The driving voltage i.e. potential between zinc sheet and steel was observed

to be very high for an impressed current mode which is unsuitable for CP of reinforced concrete resulting in debonding [46].

On the other hand, Zinc-rich paints (ZRPs) are efficiently used as an anti-corrosion paint on ferrous metals and as a substitute to hot-dip galvanizing [47,48]. They can be easily applied by roller, brush or spray and thus can be advantageous over other anodes.

Zinc anodes for protecting RC structures can be found in numerous references. However, the literature search indicated limited work on Zinc Rich Paint (ZRP) as a CP anode for concrete structures. This paper provides the first systematic electrochemical examination of ZRP as an anode system for the ICCP. This paper is a result of joint collaboration with Atkins Transportation to develop the basis of design and document electrochemical properties of ZRP for use in cathodic protection of chloride contaminated reinforced concrete structures. The primary objective of this study was to evaluate the feasibility of using ZRP as an anode for the ICCP system.

2.0 Experimental Investigation

2.1 Materials

For this research, a commercially available solvent based zinc-rich paints containing zinc powder, aromatic hydrocarbons, and a binder has been used. This paint can be applied by brush, roller, spraying, or dipping under any atmospheric condition. For now, it is not possible for authors to disclose further information regarding the paint material due to commercial confidentiality.

2.2 Specimen Preparation

All the concrete specimens of C32/40 grade were cast during the study with water cement ratio of 0.5 which is a similar grade for existing aged structures. The mix proportioning is finalized after successful trial mixing as per BS 1881-125:2013 [49]. The details of mix proportions of specimens are shown in **Table 1**. 3% NaCl solution by weight of cement was deliberately added to the mixing water during casting as specified in the NACE Standard TM0294-2007 [50]. Specimen size varied

with the type of experiment and described in the respective sections. Specimens were demoulded after 24 hours and cured in salt solution at 20±1°C for a total period of 28 days. Three specimens were tested for each test.

Table 1- Mix proportioning of concrete specimens

Mix	w/c Ratio	Water	Cement	Sand	Gravel (max 20mm)	Chloride kg/m^3
		kg/m^3				
3% chloride	0.5	180	360	640.5	1189.5	10.8

2.3 Coating Application

Various application and surface preparation methods have been explored [51], without deviating significantly from the best practice for the application of the coating on construction site and the best one is chosen here as a preferred method of application. Concrete surface was prepared by wire brushing the concrete surface for 15-20 min exposing a finer proportion of aggregates and removing the laitance layer. After surface preparation, specimen surface was cleaned for any dust using non-contaminated compressed air before coating. Then, the paint was thoroughly mixed using a high shear mixer to achieve a homogeneous liquid and then applied on the specimen surface, by a paint roller in 3 layers. The total thickness of paint was maintained in the range of 200-350μm. Each layer of the paint was allowed to atmospherically dry for a total period of 24 hours before application of the next layer.

3.0 Experimental Tests and Procedure

3.1 Bond Strength

The bond strength test was carried out using Elcometer 106/6 Adhesion equipment as shown in **Fig. 1**. Concrete cubes of size 100×100×100 mm were cast for the test. The substrate was cured in potable water for 28 days then, allowed to air dry for at least a month prior to coating and pull-off tested as recommended by ASTM D7234 – 12 [52]. After the completion of the coating, a metallic disc of 20 mm diameter was attached to the specimens by using epoxy. The bond strength test was performed after full curing of the epoxy resin i.e. after 24 hours. The bond strength was evaluated using the pull

out test method, in which the anode overlay was pulled to determine its bond with the substrate. The pull off force was manually applied on the disc until the failure of the bond was achieved.

Fig. 1- Bond strength test setup

3.2 Permeability property of coating

Permeability property of coating was measured in terms of water absorption and water vapour transmission as per BS 1062-3 [53] and BS EN ISO 7783:2018[54] respectively. For water absorption, concrete specimens of 100 mm diameter and 50 mm thickness were cured for 28 days, coated on one side only and then initial conditioned at 50±2°C temperature and 80±3% RH for 3 days. The specimens were then placed in water with the coated surface facing the water side and weight gain was measured for 7 days after placing the specimen in water. The water absorption rate was then computed as per the standard [50].

ZRP been a non-self-supporting coating, was applied on the porous substrate and tested for water vapour transmission using cup method. The cup is filled with water and the amount of moisture loss through the coating covering the mouth of the cup is measured by subsequent weighing as per the standard [51].

3.3 Polarization Test

The principle of this test is to assess the performance of ZRP coating anode for ICCP system installed to reinforced concrete elements and evaluate the following characteristics:

(i) Identify the primary conductor best suited for uniform current distribution across ZRP anode coating.

(ii) Cathodic Polarization of the steel reinforcement in concrete by the ZRP anode.

This test was carried out on three similar slab specimens of size 200×200×70 mm. Two ribbed steel bar of 10 mm diameter with allowance for 50 mm cover were embedded in the slab. The exposed length of the steel bar in contact with concrete inside the specimen was 100 mm. The exposed end of each rebar outside the mould has been covered with a heat-shrink sleeve to protect it from corrosion when the specimen is placed in water and /or salt solution. Each specimen contains one miniaturized mixed metal oxide/titanium (MMO/Ti) and one Ag/AgCl/0.5M KCl reference electrode to monitor steel/concrete/electrode potential.

For the first part of the experiment, two types of primary anode conductors were used (i) MMO Coated Titanium Mesh Ribbon and (ii) Anomet platinum clad wire. Anomet platinum clad wire is covered with a carbon fibre mat to protect it from any physical damage. The schematics of the connections are shown in **Fig. 2. Table 2** gives the total dry coat thickness (DFT) of paint on each specimen.

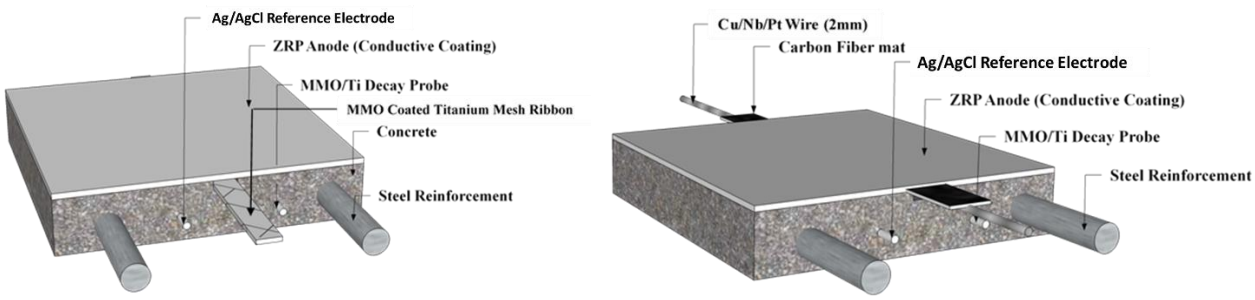


Fig. 2- Schematic of polarization test specimens with (a) MMO/Ti ribbon primary anode (b) Anomet platinum clad wire primary anode

Table 2-Dry film thickness of ZRP Coating on slab specimens

Slab	First Coat Thickness (µm)	Dry Coat Second Coat Thickness (µm)	Third Coat Thickness (µm)	Total Thickness (µm)
Slab 1	110	99	73	282
Slab 2	97	92	86	275
Slab 3	99	94	88	281

The effectiveness of the primary anode conductor was assessed by potential mapping versus an external reference electrode (Ag/AgCl/0.5M KCl) before and during polarization. This is done to

identify the most efficient primary anode conductor that can distribute current within the coating with minimum loss of voltage. The specimens were polarized at six levels of current density, i.e., 10, 20, 30, 40, 50 and 60 mA/m^2 of steel surface area, which were approximately 3.125, 6.25, 9.375, 12.5, 15.625 and 18.75 mA/m^2 of the anode surface area. The polarization and depolarization behavior of steel in concrete specimens were recorded every minute using a data logger. The polarization recorded were 'ON' potentials when the system was energised. For both polarization and depolarization tests, specimens were partially immersed in the 3% salt solution up to the rebar level in temperature and humidity controlled room since starting of the experiment. Hence, the moisture content of the samples remains constant throughout but not fully saturated. For initiating cathodic protection current in the specimen, negative terminal of the power supply was connected to the steel bars and the positive terminal to the primary anode conductor. Specimens were polarized for 5 days and then 24 hours depolarization was recorded. Each specimen was tested for each current density with decay period in between at the same time using separate power supplies to keep the environmental conditions same. The final depolarization was then analyzed to determine whether protection criterion was met in accordance with BS EN ISO 12696:2016 [37].

3.4 Service life test

The principle of this test is to get an indication of anodes ability to perform satisfactorily for a specific number of years. The test was performed in accordance with NACE TM0294 [50]. The accelerated test requires passing high current to concrete, which may lead to its premature failure, thus test was performed in an aqueous solution. The setup required is shown in **Fig. 3(a)**.

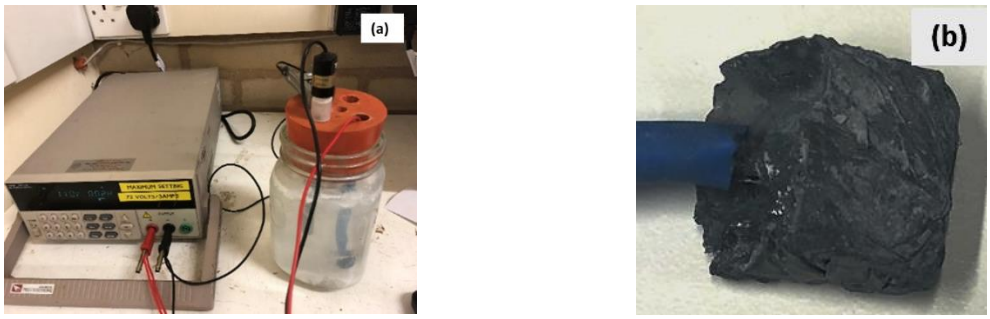


Fig. 3 (a) Setup for service life test (b) ZRP Block

A 20×20×20 mm ZRP block with Anomet platinum clad wire at the centre of the block for electrical connection was cast by filling the mould with paint and then oven dried at 40°C, as seen in **Fig. 3(b)** and used as an anode. The anode area was approximately 20 cm^{2} after drying. For the cathode, 12.7 mm diameter titanium rod was used. Test cell used was a beaker fitted with a rubber stopper at the top to hold the electrodes and reduce air contact. Saturated calomel electrode was used as a reference electrode and a 3% NaCl solution was used as an electrolyte. Two additional holes were located on the stopper, one to vent gases away from the electrical connection and other to measure the pH of the test solution.

The anode was polarized at a constant current of 17.8 mA as per standard. Parameters such as cell voltage, cell current, anode potential vs SCE reference electrode and pH of the electrolyte were recorded every minute in the data logger until anode failure which is marked by a rapid escalation in both cell voltage and anode potential. The time of failure is recorded when the anode potential increased by 4.0 V above its initial value.

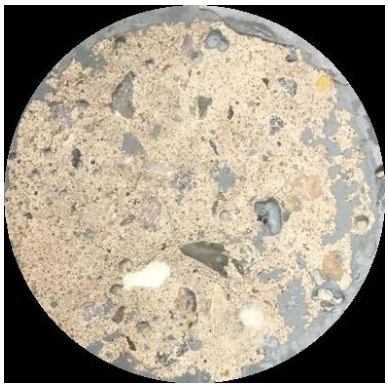
3.5 Characterization of coating and coating-concrete interface

The oxidation products formed on the ZRP block after service life was analyzed using X-ray diffraction (XRD). All the experiments were carried out at room temperature using copper radiation (Cu-Kα). The values of test parameters such as scan speed and range of 2θ were 0.03^{o}/sec and 10° to 90°, respectively. Also, Field Emission Scanning Electron Microscopy (FE-SEM) analysis was performed to study the microstructure of the coated sample and to study the zinc oxidation products formed during polarization at an accelerating voltage of 15-20kV. Samples were taken from polarization specimens after the test, grounded and cold mounted. The microstructures of the prepared samples were examined using secondary electron (SE) in a Zeiss Gemini Sigma 500VP scanning electron microscope (SEM) and EDS.

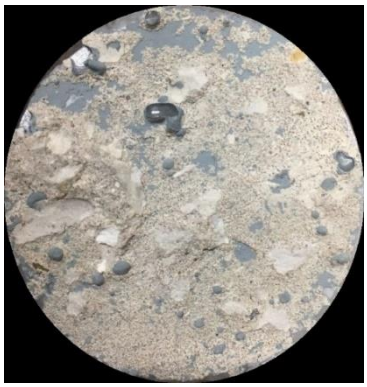
4.0 Experimental Results and Discussion

4.1 Bond Strength

For the bond strength test, both failure load and failure mode were recorded. The average pull off failure stress obtained was 2.73 MPa. This may be due to the minimal or null amount of aggregates exposed in the immediate dolly testing position in substrate preparation. The amount of aggregates exposed has a direct influence upon the pull-off strength since the bond interface between the coating and the exposed aggregate(s) is weakened due to the inherent smooth surface of the aggregate [55]. The observed pull of strength for MR substrate roughness is greater than the required value of 1.5 MPa (for flexible systems with trafficking) and 2.0 MPa (for rigid systems with trafficking) recommended by BS EN 1504-2:2004 [56]. Thus, the ZRP paint used satisfies the bond strength requirement.

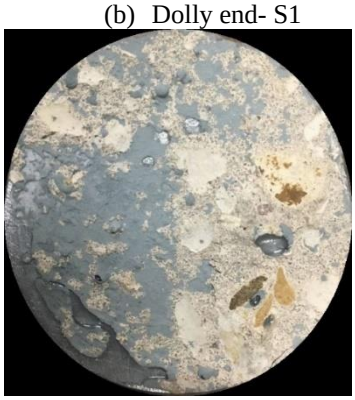


(a) Substrate end- S1

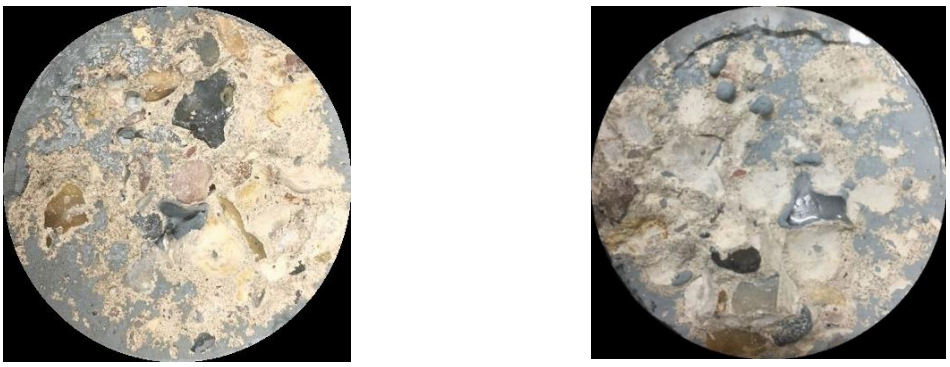


(b) Dolly end- S1

(c) Substrate end- S2



(d) Dolly end- S2



(e) Substrate end- S3 (f) Dolly end- S3

Fig. 4- Bond strength test failure mode of different surface roughness

Fig. 4 illustrates failure modes for prepared surface profile and the detailed failure mechanism is given in **Table 3**. Mode of failure is an important factor when the specimens are tested for bond strength as it gives a clear indication of the bond that occurred between the two layers. As observed in **Fig. 4**, the main failure was within the substrate giving higher bond strength.

Table 3- Bond strength and failure mode for different samples

Specimen No.	$T_{env.}$ (°C)	RH_{env} (%)	$T_{substrate}$ (°C)	DFT (µm)	σ (MPa)	σ_{av} (MPa)	Failure Type	Area of Fracture (%)
1	20.0 ±1.0	60.0 ±2.0	24.0±0.25	319	2.90	2.73	A, B/C	A = 98, B/C = 2
2			24.0±0.25	314	2.70		A, B/C	A = 95, B/C = 5
3			24.5±0.25	319	2.60		A, B/C	A = 92, B/C = 8

* $T_{env.}$ (°C) = environmental temperature, RH_{env} (%) = environmental relative humidity, $T_{substrate}$ (°C) = substrate temperature, DFT (µm) = dry film thickness, σ_{av} (MPa) = average pull-off stress, A = failure occurring within concrete substrate, A/B = failure between concrete substrate and coating, B/C = inter-coat failure, -/Y = failure between adhesive and coating

Changes in the bond strength after the polarization current is applied and any deleterious effect of acidification is outside the scope of this study.

4.2 Permeability property of coating

Table 4 shows the water absorption rate of the ZRP coating. It can be seen that the coating reduces the absorption of water by concrete. The water transmissibility of coating was found to be 0.0018 $kg/m^2.h^{0.5}$, which was 14% lower as compared to concrete without coating. The water transmissibility of coating found was less than 0.1 $kg/m^2.h^{0.5}$, hence as per BS EN 1504-2:2004 [56], coating restricts diffusion of chloride ions and capillary water absorption.

Table 4- Water absorption rate for ZRP coated and uncoated sample

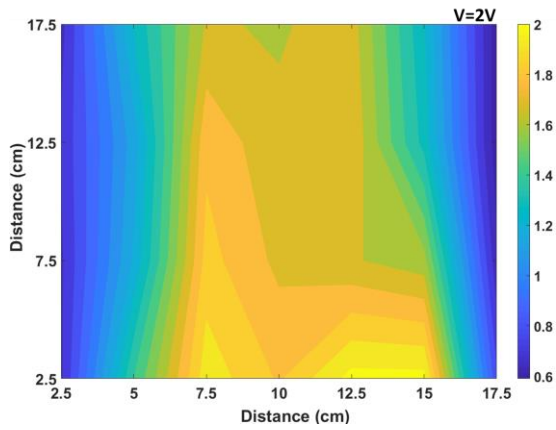
Sample	Water Absorption Rate ($kg/m^2/\sqrt{h}$)	Water Vapour Transmission (WVT)	
		WVT Rate $g/m^2/h$	Equivalent air layer thickness, s_D (m)
Uncoated sample	2.1×10^{-3}	-	-
Coated sample	1.8×10^{-3}	1.3	0.65

Performance of coating is also affected by its capability of aiding or restricting the passage of water vapour. For ZRP coating, water vapour transmission rate was found to be 1.3g/m^2/hr with an equivalent layer thickness (s_D) of 0.65m. Hence coating comes under class 1 (s_D < 5m) coating and is permeable to water vapour as per BS EN 1504-2:2004 [56]. Thus, the ZRP coating allows moisture to evaporate and prevents long term debondment and premature failure.

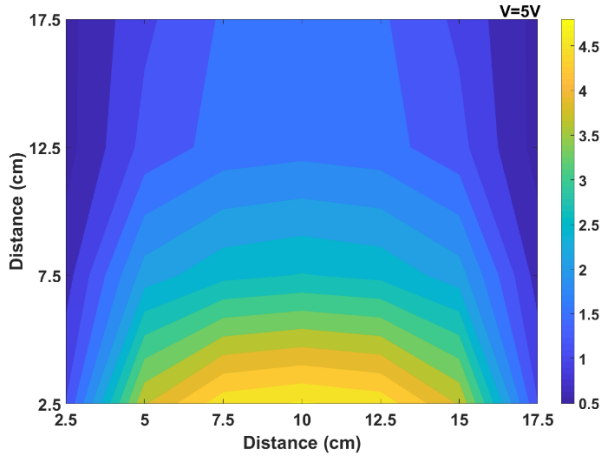
4.3 Primary Anode Selection

For reinforced concrete, the primary anode is required for most ICCP system [57]. The main purpose of the primary anode conductor is to distribute the current along the conductive coating (secondary anode). The most common primary anodes used for cathodic protection in reinforced concrete are Platinized titanium or niobium wires, Platinized mixed-metal-oxide (MMO)-coated titanium and Titanium wires or strips [57]. In this study, two types of primary anodes were used i.e. MMO coated titanium mesh ribbon and Anomet platinum clad wire. Half-cell potential drop along the secondary anode was measured by using Ag/AgCl/0.5M KCl reference electrode placed on the surface of the ZRP coating.

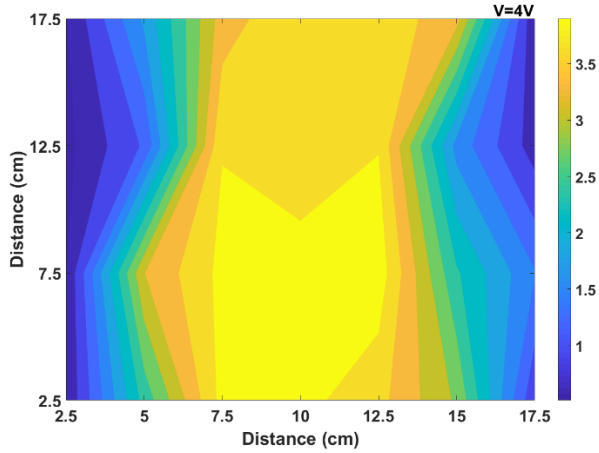
Fig. 5 and **Fig. 6** presents the contour plot for wire and ribbon primary anode conductor respectively, showing the current distribution across the ZRP coating during polarization. The applied current density during polarization was 40mA/m^2. Steel/Concrete/Electrode Potential was measured at 2.5, 5 and 7.5 cm from the primary anode on both sides. For all the specimens, more uniform current distribution is obtained by using Anomet platinum clad wire compared to ribbon anode.



(a) Sample 1

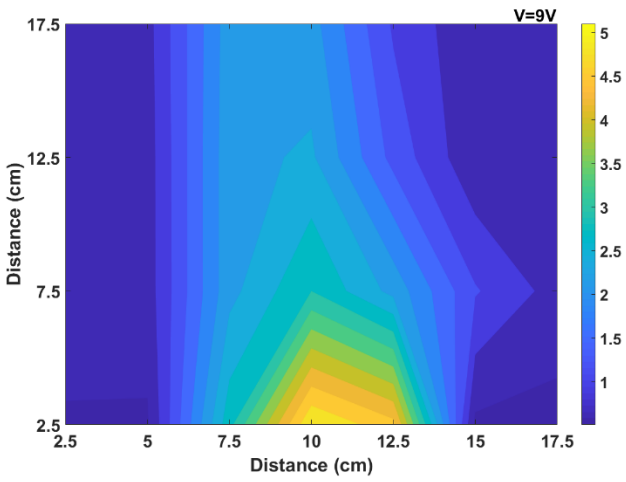


(b) Sample 2

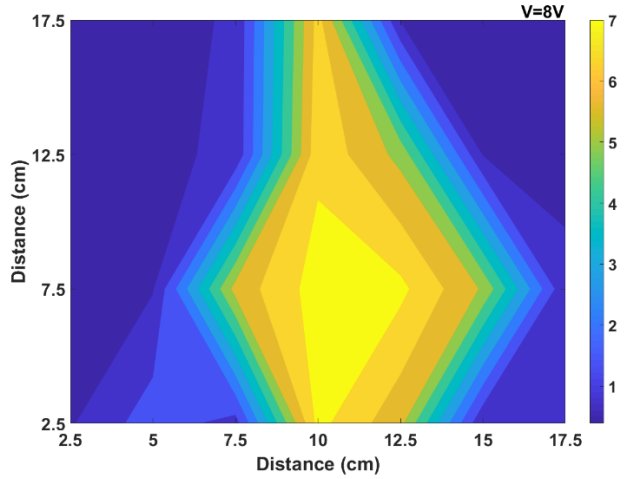


(c) Sample 3

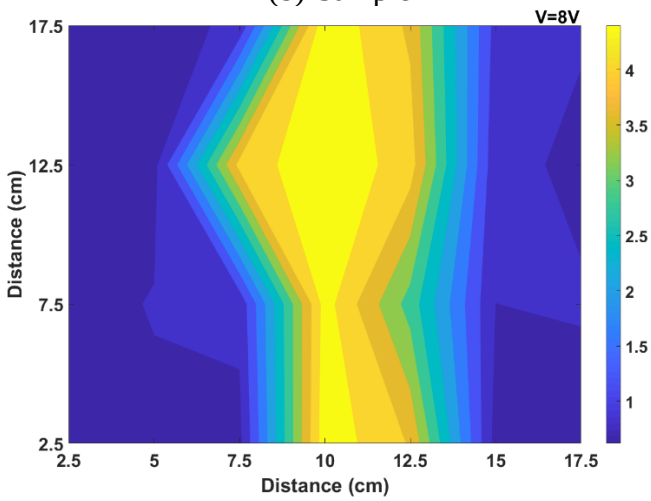
Fig. 5- Contour plots of Steel/Concrete/Electrode potential (V) across the coating before and during polarization with Anomet wire primary anode



(a) Sample 1



(b) Sample 2



(c) Sample 3

Fig. 6- Contour plots of Steel/Concrete/Electrode potential (V) across the coating before and during polarization with MMO/Ti ribbon primary anode

Fig. 7 shows percentage of the potential drop across the ZRP paint as a function of distance from the primary anode. It can be observed that in case of primary wire anode there was only 3% potential drop at 2.5cm from primary anode conductor which increased to 27.3% and 71.9% at 5cm and 7.5cm

respectively on both sides of the primary anode. Whereas in case of primary ribbon anode, at a distance of 2.5cm from the primary anode the potential dropped by almost 40%, which further reduced by 80.1% and 85.6% at 5cm and 7.5cm respectively. Moreover, the as-found voltage (V) required to achieve the current density of 40 mA/m^2 to polarize the slabs sufficiently was only 3.0 V in case of primary wire anode. MMO/Ti ribbon primary anode requires almost three times the as-found voltage as compared to primary wire anode.

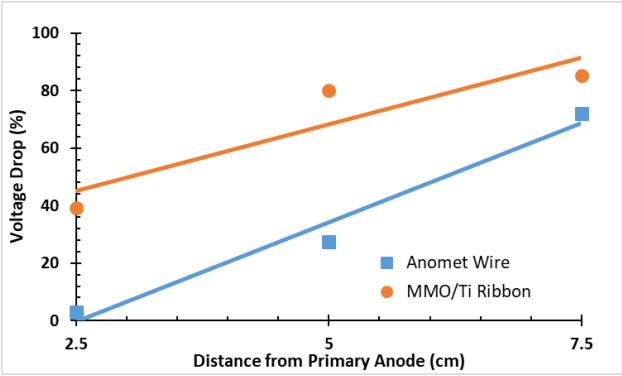


Fig. 7- Potential drop across the ZRP paint as a function of distance from primary anode

Hence, it can be observed that a reasonable current distribution could be obtained by using Anomet platinum clad wire as a primary anode conductor since it showed a more uniform current distribution with the least potential drop across the ZRP coating anode. For MMO/Ti ribbon anode, uniform coating is difficult, whereas, Anomet wire anode gives more uniform coating and better current distribution. Moreover, risk of pitting is not an issue for Anomet wire, the as-found voltage can go up to 12V. Thus, for monitoring of the efficiency and electrochemical properties of ZRP anode paint as a secondary anode for cathodic protection of steel in concrete, cathodic polarization test was carried out using Anomet platinum clad wire as a primary anode.

4.4 Polarization Test

This phase of testing involves the determination of required current density to meet the cathodic protection performance criteria as per BS EN 12696 i.e. a) 'Instantaneous OFF' potential more negative than -720 mV (vs Ag/AgCl/0.5M KCl) or b) 100 mV decay criterion over a maximum of 24

hours. The current density, 'Instant-OFF' potential, 4-hour decay and 24-hour polarization decay criteria were used to evaluate the ZRP as an anode system for ICCP system.

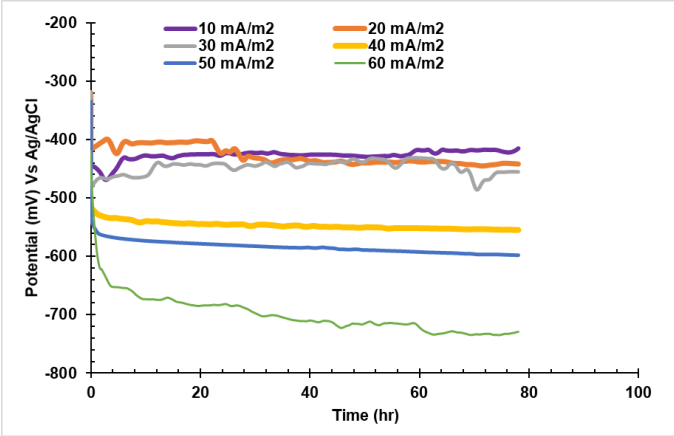


Fig.8- Electrochemical performance of specimens at various current densities with respect to Ag/AgCl/0.5M KCl electrode

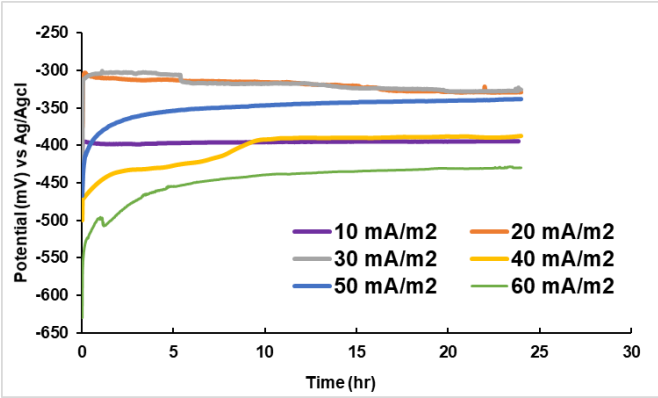


Fig. 9- Depolarization behaviour of specimens at various current densities with respect to Ag/AgCl/0.5M KCl electrode

Fig. 8 and **Fig. 9** shows the polarization and depolarization behaviour evaluation of the ZRP anode with six different current densities (10, 20, 30, 40, 50 and 60 mA/m^2 per steel surface area) [3.125, 6.25, 9.375, 12.5, 15.625 and 18.75 mA/m^2 per anode surface area] respectively. Results are summarized in **Table 5**.

Table 5- Summary of polarization test results

Current density/ steel area mA/m^2	Current density/ anode area mA/m^2	Pre energization Potential (mV)	'Instant off' potential (mV) Vs		4 hr decay (mV) Vs		24 hr decay (mV) Vs		Voltage across anode (V)
			MMO/Ti	Ag/AgCl/0.5MKCl	MMO/Ti	Ag/AgCl/0.5MKCl	MMO/Ti	Ag/AgCl/0.5MKCl	
10	3.13	-323	-462	-411	28	13	32	16	1.5-2.5
20	6.25	-320	-414	-376	60	41	67	48	2-3
30	9.38	-318	-432	-383	83	57	98	80	2.5-4
40	12.50	-300	-546	-486	94	108	130	181	3-4
50	15.63	-342	-525	-498	143	110	164	153	4-5
60	18.75	-338	-641	-630	175	168	209	200	5-7

The findings from the evaluation are summarized as follows:

- There is a significant potential rise in first 5 hours of polarization, after which potential is still rising but at a slower rate. Potential rise increases with an increase in polarization current density. The difference between 'ON' potential and instantaneous 'OFF' potential was in the range of 10-70 mV (vs Ag/AgCl/0.5M KCl).

- The average 4-hour and 24-hour decay increases as polarization current density increases. However, all the specimens met the 100 mV decay polarization criterion only when polarized with 40, 50 and 60 mA/m^2 of current density per steel surface area [12.5 and 15.625 mA/m^2 per anode surface area]. Also, even after depolarization, passivation was still not reached as observed from the results, thus not affecting the interpretation of the next current density. Anodes were tested for higher current density to see its ability to achieve and sustain the design current densities recommended in BS EN ISO 12696 at 1:1 steel: anode surface area ratio.

- **Table 5** shows voltage across the coating when a constant current is supplied through the power supply. It can be seen that for all current densities used, the as-found voltage (V) across the anode was below 10V. The as-found voltage increases with an increase in supplied current density and showed a similar trend as decay values. At a current density of 40 mA/m^2, the average as-found voltage across the anode was 3 V.

- **Fig. 10** shows that the optimized current density required for successful application of ZRP as an anode for ICCP is 40mA/m^2 of steel surface area, equivalent to 12.5 mA/m^2 of anode surface area, meeting BS EN 12696 [37] criterion (b). 40mA/m^2 is equivalent to 17.2kC/m^2 of charge passed, which is quite less than 50kC/m^2 required to stop corrosion [6]. However, it still satisfies the 100 mV decay criterion which is the main aim of the test. For atmospherically exposed concrete polarized for a longer period of time, this could be met with lower current density due to reduced corrosion rate as a result of higher concrete resistivity and lower moisture content in dry conditions.

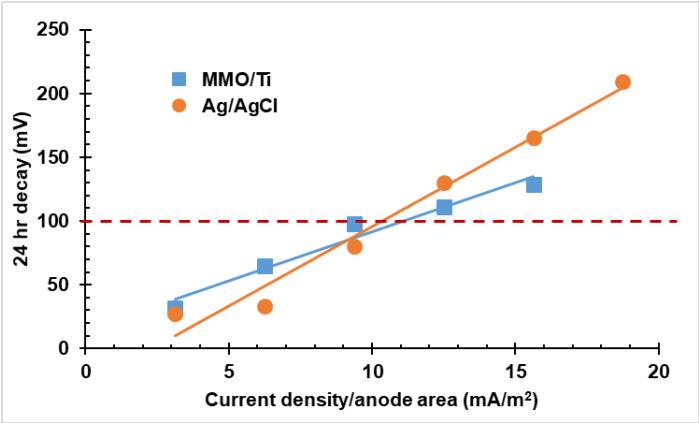


Fig. 10- Correlation between potential decay over 24 hours and polarization current density

- **Fig. 11** shows the correlation between 24 hour decay and Steel/Concrete potential shift w.r.t. MMO/Ti (R^2 = 0.96) and Ag/AgCl/0.5M KCl reference electrode (R^2 = 0.94) and showed a quadratic relationship between the two. Higher the potential shift, higher is the decay. From the graph, it can be calculated that for 100 mv 24 hour decay and considering the tested specimen age and conditions, at least 98.8 mV (vs Ag/AgCl/0.5M KCl) of potential shift over a period of 4 days is required. In practice, long term polarization may be needed.

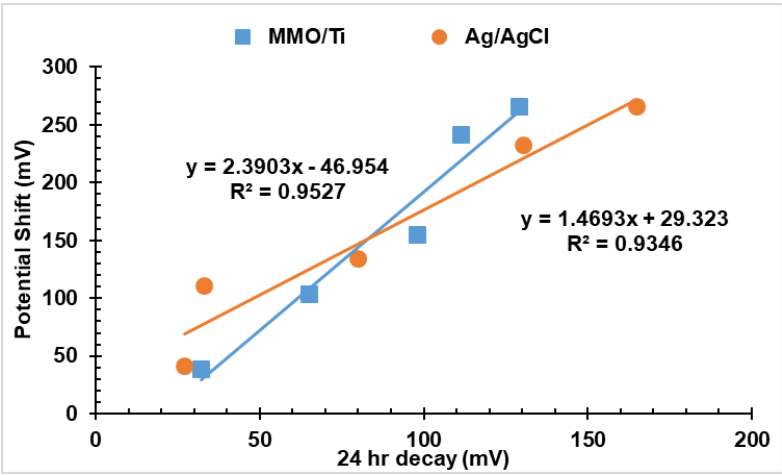


Fig. 11- Correlation between potential decay over 24 hours and Steel/Concrete potential shift

4.5 Service Life Test

Anode was polarized at a constant current of 17.8 mA until anode failure, which is marked by an increase of anode potential by 4.0 V above its initial value. Results are shown in **Table 6**. Total time of polarization before failure was 12 days. Moreover, the pH of the test solution changed from 8.5 to 11.8 during the polarization period, indicating formation of some oxides or hydroxides.

Table 6- Results of Anode Life Testing in 30 g/L NaCl Solution

Test	Time	Cell current (mA)	Cell voltage (V)	Anode potential vs SCE (V)	pH
Reverse Current	1 min	-17.00	1.28		
	1 h	-17.28	1.23		
	8.8 h	-17.91	1.11		
Normal Current	1 h	-17.81	-0.70	0.91	8.5
	1 day	-17.85	-0.79	0.78	-
	2 days	-17.80	-1.01	0.37	-
	3 days	-17.91	-1.60	-0.21	-
	4 days	-17.50	-2.21	-0.82	-
	5 days	-16.60	-2.88	-1.55	-
	6 days	-17.30	-4.39	-2.98	-
	7 days	-17.18	-4.34	-2.99	-
	8 days	-17.18	-4.31	-2.97	-
	9 days	-17.34	-4.33	-2.98	-
	10 days	-18.56	-4.40	-3.07	-
	11 days	-17.56	-4.38	-3.03	-
	12 days	-18.81	-4.41	-3.04	11.8

Using data in **Table 6** and equation Q = it, where *Q* is the total amount of charge passed, *i* is applied current density and *t* is time, it can be estimated that when anode is operated at 20 mA/m^2 current density, it will perform satisfactorily up to approximately 15 years. The typical service life of currently commercially available paint anode system is 15-20 years based on its physical detachment from the surface without considering anode consumption. Hence, the service life of ZRP anode is comparable. At the end of the test, the ZRP block was examined, as shown in **Fig.12**. It can be observed that the whole ZRP block was covered with a white product. The powdered sample of the white product was collected, dried and tested using XRD and XRF. XRF analysis showed that the major component being zinc oxide (**Table 7**).

Fig. 12- White product observed on ZRP block at the end of anode life testing

Table 7- XRF Analysis of white product

Main Component	Wt. %
ZnO	77
Na_2O	6
Cl	17

Fig. 13 shows the X-ray diffractograms of the product. Zinc oxide and Zinc hydroxyl chloride hydrate are identified from these specimens. Peaks corresponding to 42.3^0, 13.0^0 of 2Θ are identified, which corresponds to zinc oxide and zinc hydroxyl chloride hydrate respectively. This confirms zinc in the paint is oxidising to form zinc oxide/hydroxides during polarization. This might affect current and potential distribution in the long run. Further, extensive durability testing is under study to determine ZRP performance before this coating is considered as a viable product.

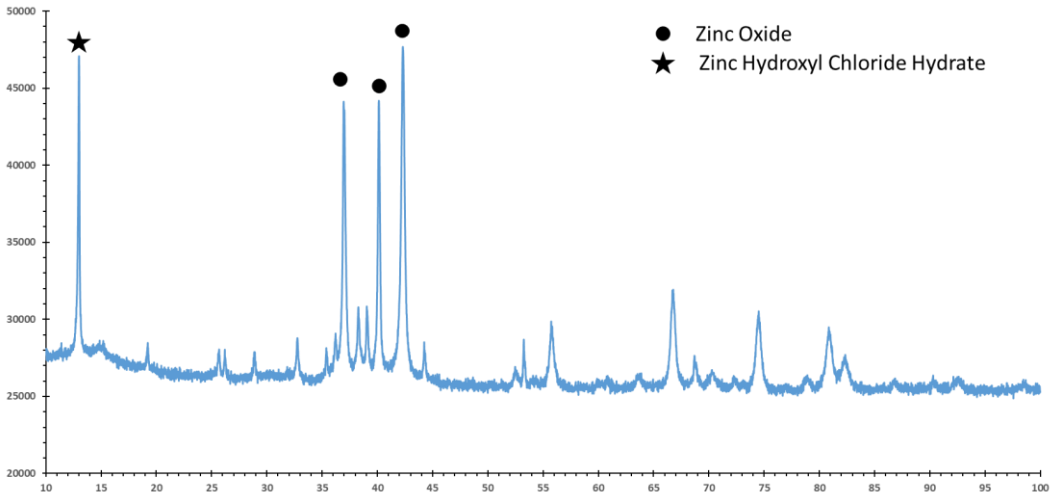
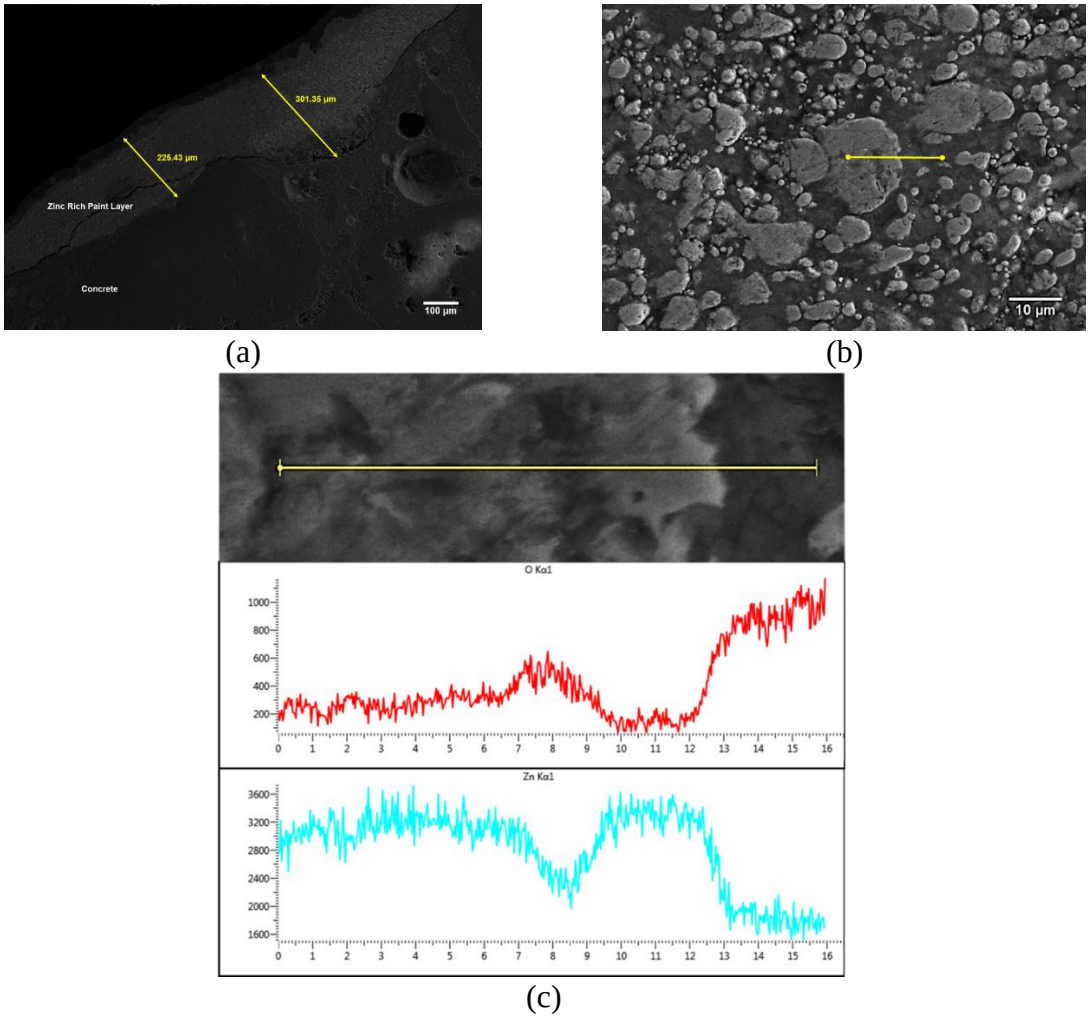


Fig. 13- XRD analysis of white product

4.6 Microstructural Analysis

Coated concrete samples were collected after the polarization test on slabs and analysed using SEM/EDS. **Fig.14(a)** shows SEM micrographs of ZRP-concrete interface after polarization, depicting coating thickness between 200-350µm. **Fig.14(b)** shows a cross section of the coating sample, in which zinc corrosion products on the surface of zinc particles were observed. A line scan analysis was performed on one of the particles and results are shown in **Fig.14(c)**, which shows that the zinc corrosion products were mainly composed of zinc and oxygen, suggesting the formation of zinc oxide or zinc hydroxide. This could be due to the self-corrosion process of zinc particles (i.e.

zinc dissolution and oxygen reduction reaction occurred on the surface of zinc particles) at zinc/electrolyte interface [58].



(a) (b)

(c)

Fig.14- Cross- sectional analysis of ZRP concrete (a) cross-section of SEM micrograph (b) cross-section of coating sample (c) line scan analysis

Fig. 15 shows surface analysis of ZRP coated concrete samples from the coated side. Several small hexagonal plates were observed, The EDS analysis of yellow marker in **Fig. 15(b)** is shown in **Fig. 15(c)**, depicting main peaks of zinc and oxygen, again suggesting the formation of ZnO. Similar morphology was observed by Perkins and Bornholdt [59]. Surface charging by the electron beam was observed to a varying degree, but generally was not a serious problem.

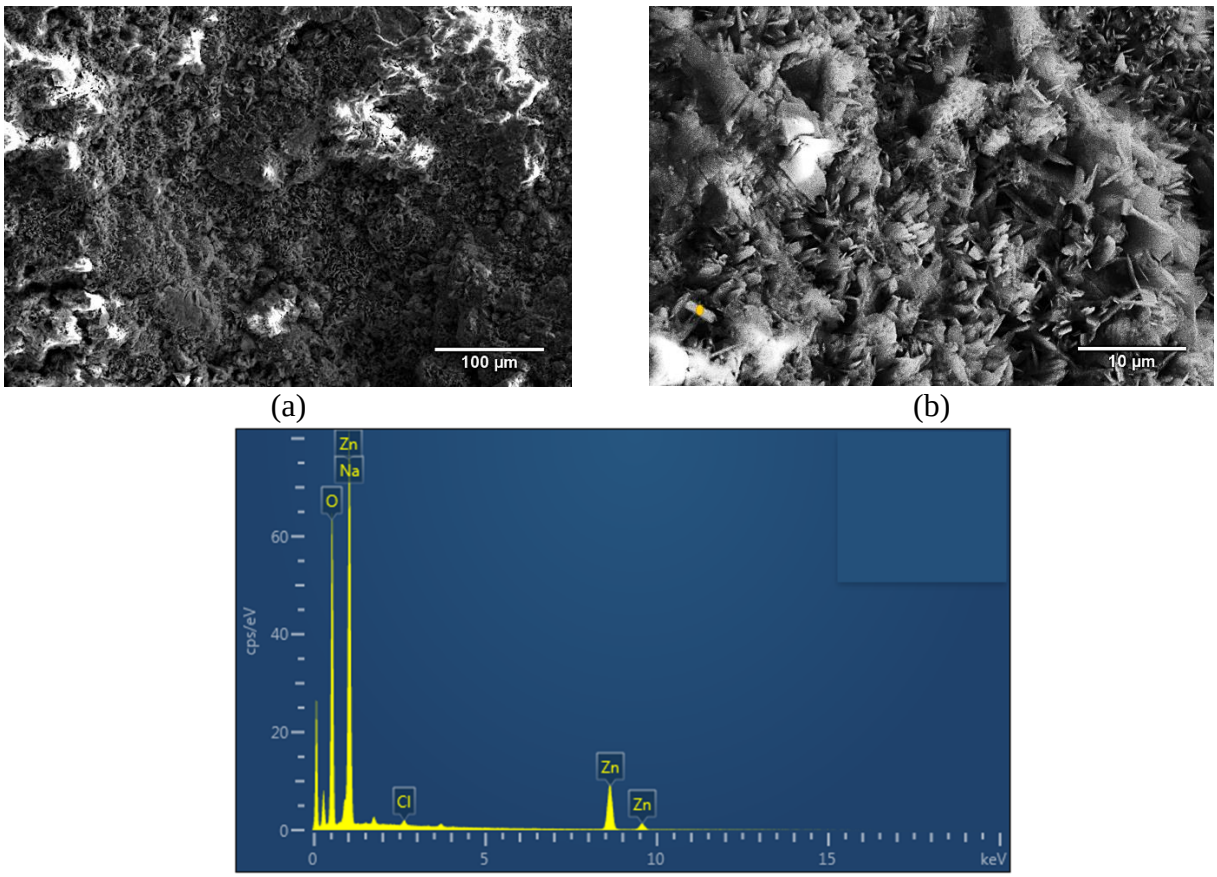


Fig. 15- SEM micrographs of surface analysis of coated sample at different magnifications (a) and (b). (c) shows corresponding EDS spectra of yellow marker in (b)

5.0 Summary and Conclusions

The research presented in this paper evaluates the feasibility of using ZRP as an anode of an ICCP system. Following conclusions can be drawn from the study:

- Results of electrochemical testing showed that ZRP conductive coating can be used successfully as an effective ICCP anode system and satisfy the performance criteria in accordance with BS EN ISO 12696 [37] standard.

- The ZRP coating showed satisfactory bond at the anode-concrete interface. The pull-off failure stress was 2.73 MPa satisfying the recommended required pull off strength according to BS EN 1504-2:2004 [56].

- More uniform current distribution with the least potential drop across the ZRP coating anode was obtained by using Anomet platinum clad wire primary anode when compared to MMO coated Ti ribbon anode.

- Permeability results showed ZRP coating to be water vapour permeable, thus preventing long term debondment and premature failure.

- Polarization results showed satisfactory performance of the ZRP anode with an optimum current density of 12.5 mA/m^2 per anode surface area. The results satisfy 100 mV depolarization criterion i.e. criterion (b) of BS EN 12696 [37].

- Anode was even capable of sustaining design current densities recommended in BS EN ISO 12696 at 1:1 steel: anode surface area ratio.

- The service life of anode was estimated from the accelerated service life test to be 15 years when operated at 20 mA/m^2 current density.

- Microstructural analysis showed the formation of oxide/hydroxide products of zinc after polarization. This might affect current and potential distribution in the long run.

- Further, extensive durability testing and comparison to other anodes such as carbon pigmented paints are required to determine ZRP performance before this coating is considered as a viable product and same is under study by authors.

6.0 References

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Declaration of Interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.