

Electrochemical process to improve the durability of concrete structures



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ABSTRACT

Chloride induced corrosion of steel in concrete is a major threat to the construction industry leading to the premature failure of concrete structures. Electrochemical injection of corrosion inhibitor (EICI) into concrete is a promising technique for existing concrete structures, which can serve as a rehabilitative measure to retard or reduce rebar corrosion. An attempt has been made to evaluate the effectiveness of a hybrid inhibitor formulation injected into chloride contaminated concrete. The optimised current density of 0.5 A/m² was found to be a minimum requirement with maximum efficiency. During EICI, the amount of free chloride removed from cover concrete was also tested. The mechanism of inhibitive action was established through FTIR, SEM, EDAX and MIP studies.

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1. Introduction

Reinforcing steel embedded in a chloride-free Portland cement concrete exhibits a high degree of resistance to corrosion. The cement paste in the concrete provides an alkaline environment that protects steel against corrosion. This corrosion resistance is due to passivating or protective ferric oxide film that forms on the steel when it is embedded in fresh concrete. This film is stable in the highly alkaline concrete environment that has a pH of approximately 12–13. In the passive state, steel is protected by the naturally high pH and availability of oxygen in the concrete. The corrosion rate of steel in this state is negligible. The factors influencing depassivating forces are carbonation and penetration of chloride ions [1–3]. Corrosion steel is an electrochemical process. Two requirements are necessary for the development of a corrosion cell. Sufficient dissolved oxygen is required for reaction at the cathodic sites and moisture is required to maintain low electrical resistivity in the concrete between the anode and cathode. Anodes and cathodes on either a macro or micro scale develop, creating a corrosion cell. Micro cells occur within millimetres of each other, while macro cells may be upto several metres apart. In a corrosion cell, metallic iron corrodes or oxidizes at anodic sites to form ferrous ion with the release of two electrons and the reaction is shown in Eq. (1).



Electrons flow through the steel to combine with oxygen and moisture at the cathode to form hydroxyl ions as shown in Eq. (2).



Hydroxyl ions then combine with a ferrous ion at the anode to form ferrous hydroxide as shown in Eq. (3).



This ferrous hydroxide can react to form ferric hydroxide $\text{Fe}(\text{OH})_3$ and ferric oxide Fe_2O_3 in the presence of water along with other species. The implication of these reactions is that the corrosion products occupy a greater volume than does the original steel. The resulting tensile stress may be sufficient to cause cracking or spalling if these stresses exceed the tensile strength of the concrete. The effect of chloride inclusion in concrete is two fold: it increases the conductivity of the concrete and acts as a catalyst in the oxidation of iron. In the presence of chloride ions, intermediate reactions may occur involving iron chloride.

Chlorides are not consumed in the corrosion process but simply act as catalysts at the anode. The corrosion reaction rate is therefore controlled by the supply of water and oxygen to the cathode. Thus, even though a concrete deck may be sealed to prevent new chloride ingress into the slab, continued chloride-induced corrosion may occur. The reaction produces hydrogen ions at the anodic site resulting in a lowering of the pH and creating more favourable corrosion conditions by destroying the passive layer. Under these conditions the presence of molecular oxygen is not a requirement since the oxygen needed to develop ferrous oxide may be developed from the water itself. Again, the ferrous

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oxides developed may continue reacting to form other products such as ferrous and ferric chloride. These products may occupy an even greater volume than those of the ferrous and ferric hydroxides. At the cathode, different reactions may occur depending on the availability of oxygen. The balancing reaction that occurs at the cathode for corrosion in the absence of oxygen is as shown in Eq. (4).



In the presence of oxygen, the reactions at the cathode are shown in Eqs. (2 and 5).



In both instances, steel at the cathodic site is protected against corrosion. Corrosion in concrete requires an anode, cathode and electrolyte. Chloride in concrete acts as an electrolyte, increasing the level of conductivity as chloride ions increase. It also de-passivates the steel reinforcement. The level of chloride ion required to initiate corrosion in concrete corresponds to 0.15% soluble chloride ion by weight of cement. This value refers to the amount of water-soluble chloride rather than the total chloride. If chloride is present during the curing process, some chloride ions become chemically bound in the hydration products and are therefore not available in solution to act as a catalyst. Chlorides may be present in slakes where calcium chloride is used as an accelerator to setting. Also, in areas near the sea or with brackish groundwater, chloride may have entered the concrete through contamination of the aggregate. If only low chloride concentrations are present, they may become bound during the hydration process. Corrosion of steel in concrete can be mitigated by adopting various preventive measures viz., cathodic protection, using corrosion inhibitors, coating to steel rebar, coating to concrete, using blended cements, realkalization of concrete etc., [4–7]. The use of corrosion inhibitors is the more economical and appropriate method of protection for concrete structures subjected to reinforcement corrosion [8–11]. In concrete, chloride and inhibitor ions travel through natural diffusion, electro migration, and through external pressure gradient [12]. Surface applied corrosion inhibitors is relatively economical and their application is found to be very easy and efficient [13–15]. Applications of electrochemical treatments include mainly the electrochemical realkalization, electrochemical chloride extraction (ECE), electrochemical injection of corrosion inhibitor (EICI) and cathodic protection [16,17]. In EICI, a current density of $1\text{--}5 \text{ A m}^{-2}$ is usually applied between embedded steel as cathode and an external anode placed on the concrete surface in an aqueous solution containing the relevant inhibitor for a few weeks [18–21]. During the application of current, chloride ions migrate out of concrete towards the external anolyte solution, while EICI was shown to be an effective method of preventing corrosion in existing structures, and this can serve as a rehabilitative measure to retard or reduce corrosion. In the present investigation, a hybrid inhibitor formulation was designed and used for EICI studies at an optimised constant current density of 0.5 A m^{-2} . The efficiency of the inhibitor formulation was evaluated by conducting various electrochemical studies. The study showed that such inhibitor injection could provide adequate corrosion protection to rebars embedded in even chloride contaminated concrete.

2. Experimental

2.1. Materials used

Ordinary Portland cement (OPC) of grade 53 was used for the casting the specimens. Local clean river sand (fineness modulus of medium sand equal to 2.6) conforming to grading zone III of ASTM standards was used. Locally available aggregates conforming to graded aggregates of normal size greater than 8 mm and less than 20 mm of ASTM standard was used. Potable water has been used for making concrete specimens. The water is free from oils, acids and alkalis. As per IS 456-2000, the permissible limit for chloride is 500 mg/l. Thermo mechanically treated (TMT) rebar of 12 mm diameter and length 560 mm was used for weight loss and open circuit potential measurements.

2.2. Inhibitors formulation

The hybrid inhibitor formulation consists of guanidine carbonate ($\text{C}_2\text{H}_{10}\text{N}_6 \cdot \text{CH}_2\text{O}_3$), thiosemicarbazide ($\text{CH}_5\text{N}_3\text{S}$), ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$), and triethanolamine ($\text{C}_6\text{H}_{15}\text{NO}_3$) (AR grade, Alfa Aesar was used).

2.3. Casting of concrete specimens

Concrete slab of size $60 \text{ cm} \times 60 \text{ cm} \times 10 \text{ cm}$ thickness were cast using OPC. 12 mm diameter and 560 mm length, of rebars were embedded with a concrete cover thickness of 25 mm. Concrete specimens were cast using 1:1.56:3.36 mix [cement: 372 kg/m³; sand: 580 kg/m³; coarse aggregates: 1245 kg/m³ with w/c ratio of 0.55]. During casting, the specimens were mechanically vibrated. After 24 h, the specimens were demoulded and cured for 28 days in distilled water to avoid any contamination. After curing, the chloride ion is allowed to penetrate into the concrete over a period of 90 days by means of alternate wetting and drying cycles of 3 days of wet in 3% NaCl and 4 days drying at room temperature. Concrete slab specimens were given enough time to induce accelerated corrosion of steel due to aggressive chloride ion.

2.4. Electrochemical injection of corrosion inhibitor (EICI) process

Fig. 1 shows the electrical circuit of EICI process on the concrete slab. Here rebar act as cathode and stainless steel plate act as anode. A special gauge made of sponge was placed in between

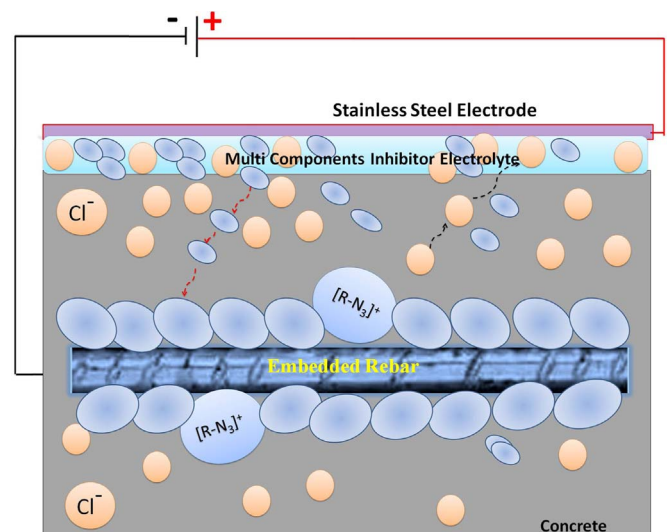


Fig. 1. Arrangement of EICI process on concrete slab.

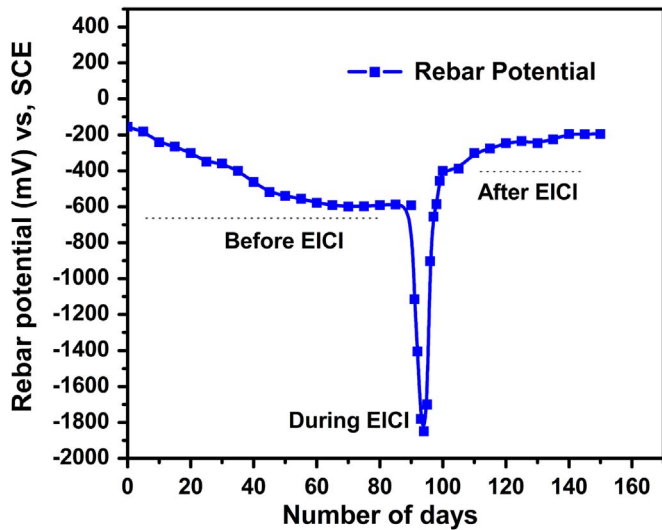


Fig. 2. Potential-time behaviour of steel in concrete before and after EICI treatment.

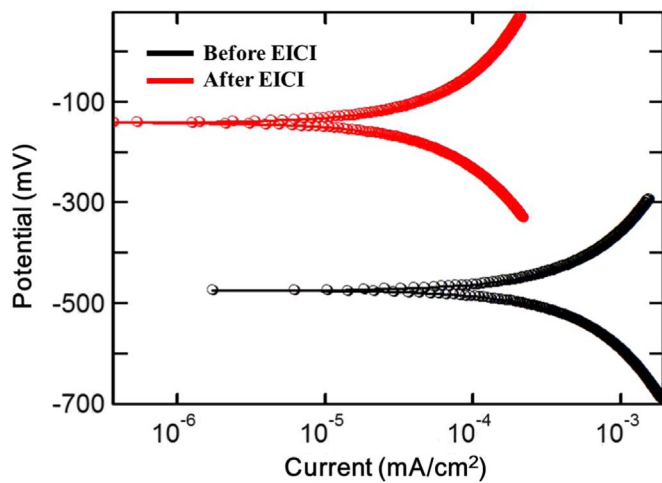


Fig. 3. Potentiodynamic polarization curve for before and after treatment of EICI embedded rebar in concrete.

anode and cathode wetted with hybrid inhibitor solution such as (0.1 M Guanidine carbonate ($C_2H_{10}N_6 \cdot CH_2O_3$), 0.1 M Thiosemicarbazide (CH_5N_3S), 2.0 M Ethyl acetate ($CH_3COOC_2H_5$), 2.0 M Triethanolamine ($C_6H_{15}NO_3$)) and EICI was carried out at a current density of 0.5 A m^{-2} with respect to steel. The gauge was continuously replenished to maintain wet condition with inhibited formulation.

2.5. Evaluation of EICI

2.5.1. Open circuit potential (OCP)

OCP of steel was monitored before and after EICI treatment regularly as per ASTM C-876.

2.5.2. Potentiodynamic polarization studies

Potentiodynamic polarization studies were carried out to

Table 1

Polarization parameters for the corrosion of steel embedded in concrete before and after EICI treatment.

System	E_{corr} (mV vs. SCE)	B_a (mV dec^{-1})	B_c (mV dec^{-1})	I_{corr} (mV cm^{-2}) $\times 10^{-4}$	C.R (mmpy) $\times 10^{-3}$	% reduction in CR
Before EICI	-474	119	99	1.424	1.650	-
After EICI	-142	108	107	0.178	0.207	87.45

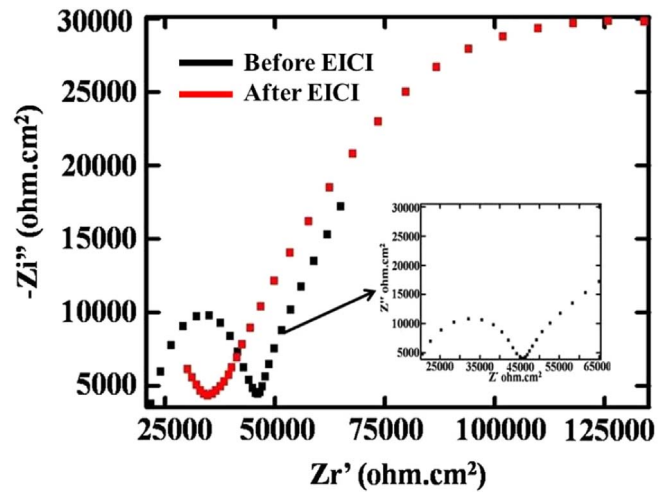


Fig. 4. Impedance plot for steel in concrete before and after EICI treatment.

Table 2

Impedance parameters for the corrosion of steel embedded in concrete before and after EICI treatment.

System	R_{ct} ($\Omega \text{ cm}^2$) $\times 10^4$	I_{corr} (mV cm^{-2}) $\times 10^{-3}$	C.R (mmpy) $\times 10^{-2}$	% reduction in CR
Before EICI	1.943	1.343	1.556	-
After EICI	10.10	0.258	0.299	80.78

Table 3

Gravimetric weight loss data for the corrosion of steel embedded in concrete before and after EICI treatment.

System	C.R (mmpy) $\times 10^{-2}$	% reduction in CR
Before EICI	2.661	-
After EICI	0.345	87.03

evaluate the corrosion kinetic parameters before and after EICI treatment by using surface mounted electrode (guard ring). Both cathodic and anodic polarization curves were recorded potentiodynamically using ACM Instruments, UK. The potentiodynamic conditions correspond to a potential sweep rate of 1 mV min^{-1} and potential ranges of $+0.2$ to -0.2 V (vs. SCE) from the OCP. All the experiments were carried out at a constant temperature of $32 \pm 1 \text{ }^\circ\text{C}$. For comparison, polarization was also carried out for the control system (specimen before EICI).

2.5.3. A.C. Impedance measurements

Similarly, impedance measurements were also carried out on before and after EICI specimens. The same three electrode cell assembly was used here also. The real part (Zr') and imaginary part ($-Zi''$) of the cell impedance were measured for various frequencies (30 kHz–10 mHz). Plots of $-Zi''$ vs. Zr' were made. For comparison, impedance measurements were also carried out for the control system (specimen before EICI).

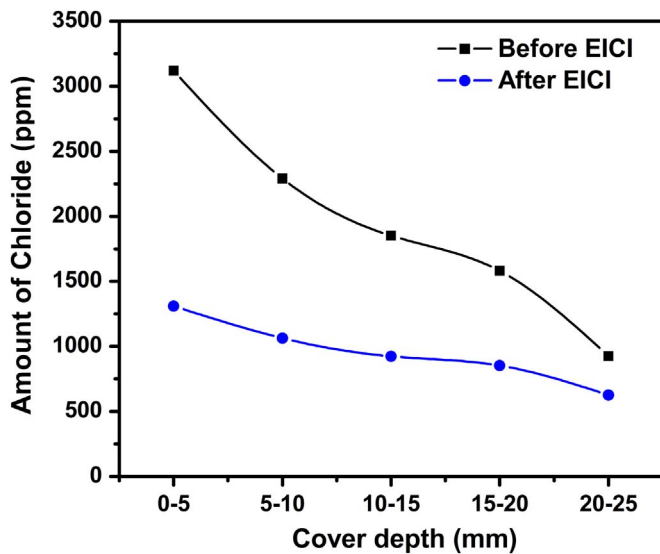


Fig. 5. Amount of free chloride contents in various cover depth of concrete before and after EICI treatment.

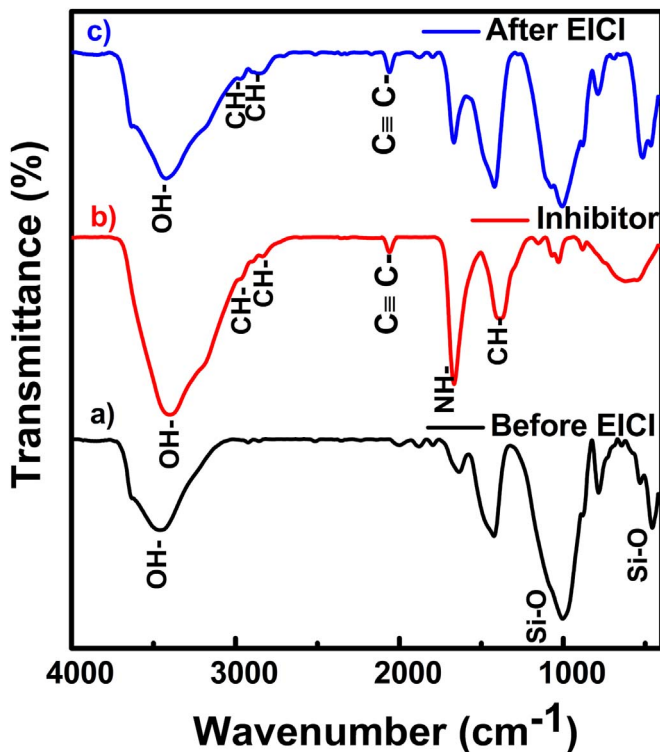


Fig. 6. FTIR spectrum for inhibitor solution before and after EICI treatment.

2.5.4. Gravimetric weight loss method

At the end of the exposure period, the concrete cubes were split open and the rebar samples were carefully taken out. Then all the rebar were pickled in inhibited hydrochloric acid to remove the rust and final weight of the rebar were measured. From the initial and final weight, the loss in weight due to corrosion was determined by the Eq. (6).

$$\text{Corrosion rate} = 87.6 W/DAT \quad (6)$$

where W is the weight loss (mg).

D is the density of the material used (g.cm⁻³).

T is time duration (h) and,

A is the area of the steel (cm²).

2.5.5. Estimation of chloride profiles

Cylindrical concrete core was drilled on the slab. Using slice cutter, at 5 mm thickness, concrete slices were cut. Then the concrete slices were crushed to powder. The powder sample was subjected to free chloride analysis [22]. The chloride contents were analysed for before and after EICI specimens.

2.5.6. Surface examination

The concrete specimens near the steel-concrete interfacial region were collected, crushed into powder and was characterised by FTIR spectra in mid IR region of 400–4000 cm⁻¹. The spectrum was recorded using ATR (attenuated total reflectance) technique. The sample was directly placed in the KBr crystal and the spectrum was recorded in the transmittance mode.

Scanning electron microscopy images were obtained using HITACHI Model S-3000H at various magnifications to study the surface morphology of the embedded steel and concrete before and after EICI treatments. Rebar and concrete samples were cut into the size of 0.5 cm² and examined by scanning electron microscopy (SEM).

Porosity of concrete specimen has analysed by mercury intrusion porosimetry (MIP, Quantachrome, PM60GT-18, USA) technique. When preparing samples for MIP test, aggregates were avoided from sampling and about 1 cm³ volume (0.4–0.6 g) have placed in quanta chrome porosity analyser and sample was used for each measurement. The instrument was capable of minimum intruding pressure of 20 mmHg, and a maximum of 414 MPa. Thus, the corresponding range of pore diameters was between about 320 μm and 20 Å. The intruded volume could be read to an accuracy of ± 0.001 cm³.

3. Results and discussion

3.1. Potential-time behaviour of steel in concrete

Fig. 2 shows the potential-time behaviour of rebar embedded in concrete before EICI, during EICI and after EICI treatments. Before EICI, the rebar potential was found to be less than –200 mV vs. SCE indicating the passivity of steel in concrete. Due to alternate wetting and drying cycles (for 90 days) the potential of steel was shifted to –600 mV indicating more than 90% probability of corrosion. During EICI (for 7 days), the embedded steel reached > –1800 mV vs. SCE due to applied electro motive force. After EICI (applied current density is switched off) then the embedded steel showed –195 mV vs. SCE indicating the perfect passive condition of the steel rebar throughout the exposure. Here it was interesting to note that EICI treatment has an effective approach to shift the potential of steel from corrosive region to passive region.

3.2. Potentiodynamic polarization studies

Fig. 3. shows the potentiodynamic polarization curves for steel in concrete before and after EICI treatment. The corrosion kinetic parameters derived from the Tafel plots are given in Table 1. It was observed from the Fig. 3 that, system with EICI treatment shifted the Tafel plot towards anodic region. Further there was a larger shift i.e more than 300 mV in corrosion potential values. For example E_{corr} value for steel in concrete before and after EICI treatment was found to be –474 mV and –142 mV respectively. With the result, the corrosion rate of rebar also considerably reduced after EICI. For example, the corrosion rate was 1.650 × 10⁻³ mmpy (before EICI) and 0.2067 × 10⁻³ mmpy (after EICI). Potentiodynamic polarization studies clearly bring out the fact that within 7 days of exposure, injected inhibitor is able to reach the steel and thereby prevent the corrosion of steel in concrete.

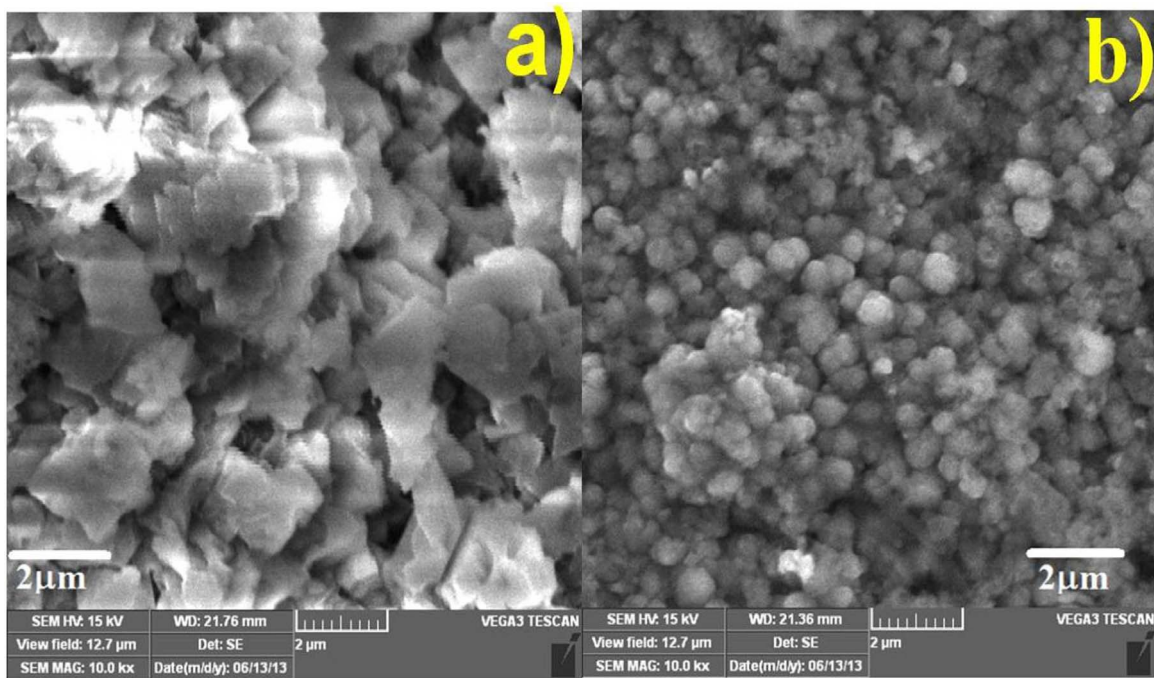


Fig. 7. SEM images for concrete specimen before and after EICI treatment.

3.3. Electrochemical impedance spectroscopy

The typical Nyquist plots obtained for steel embedded in concrete before and after EICI treatment are shown in Fig. 4. The impedance parameters are given in Table 2. It is interesting to note that system with EICI treatment showed 5 fold increase in R_{ct} values when compared to system without EICI treatment. For example the R_{ct} values are $1.943 \times 10^4 \Omega \text{ cm}^2$ and $10.100 \times 10^4 \Omega \text{ cm}^2$ for system before and after EICI respectively. EICI treated specimens showed lower magnitude of corrosion current (I_{corr}) when compared to control specimens. Here it was concluded that EICI treatment significantly reduced the corrosion rate of steel in concrete and proved to be better mitigation technique to arrest the corrosion of embedded steel in chloride contaminated concrete within a shorter period of time. The same observation was also noticed in potentiodynamic polarization studies.

3.4. Gravimetric weight loss method

The corrosion rate is calculated from the gravimetric weight loss method were given in Table 3. It was observed from Table 3 that, corrosion rate of steel in concrete after EICI treatment showed lower values than before EICI. The corrosion rate of steel in concrete before and after EICI was found to be 2.661×10^{-2} mmpy and 0.345×10^{-2} mmpy respectively. Further, 87% reduction in the corrosion rate was observed during EICI treatment.

The better performance of the designed inhibitor formulation is due to the following reason. It was a fact that amino compounds that act as corrosion inhibitors for steel in aqueous solutions undergo protonation to form cationic species, to a degree governed by their acid dissociation constants (pKa) and the solution pH. In this investigation when concrete is subjected to electrolysis between an anode placed on the external surface of the concrete and the embedded rebars acting as cathode, the migration of cationic corrosion inhibitors contained in the electrolyte solution surrounding the anode may be promoted.

3.5. Estimation of free chloride contents before and after electro injection process

Before EICI treatment, the free chloride contents estimated varied from 3120 ppm to 925 ppm. These data showed a gradual decrease of free chloride contents from the top of the slab to bottom with respect to cover depth (mm). After EICI treatment, the free chloride contents estimated varied from 1309 ppm to 624 ppm with respect to cover depth. It was observed from Fig. 5 that the free chloride content is found to be minimum (≈ 650 ppm) at a cover depth of (20–25 mm) where the rebars are placed when compared to the top surface. These data clearly proved that free chloride at the steel-concrete interfacial region moved outwards. During EICI treatment, due to applied emf the free chloride ions moved towards the anode surface. In other words, the negatively charged chloride ions migrated towards the positively charged anode surface. This is an additional advantage of EICI treatment not only reduces the corrosion of steel in concrete but also removed a considerable amount of chloride from concrete.

3.6. Surface examination

3.6.1. FTIR spectroscopy

The FTIR spectrum of concrete sample collected at the steel-concrete interfacial region before and after EICI treatment is given in Fig. 6a and c respectively. The FTIR spectra for designed inhibitor formulation are given in Fig. 6b for a comparison. The peaks observed at 1661 cm^{-1} , 1367 cm^{-1} , 2046 cm^{-1} , 2845 cm^{-1} and 2966 cm^{-1} were corresponding to $-\text{NH}_2$, C–H bending modes, $\equiv\text{C}$, and C–H stretching vibrations. Before EICI, the analysis indicated only peaks at 994 cm^{-1} , 525 cm^{-1} , 458 cm^{-1} , 3447 cm^{-1} and 1674 cm^{-1} corresponding to Si–O asymmetric stretching vibration of C_3S and/or C_2S , out of plane Si–O bending (ν_4) and in plane Si–O bending (ν_2), O–H and bending vibrations of portlandite $\text{Ca}(\text{OH})_2$ respectively. After EICI treatment, the analysis indicated that the functional group of the inhibitors namely $-\text{NH}_2$, C–H and

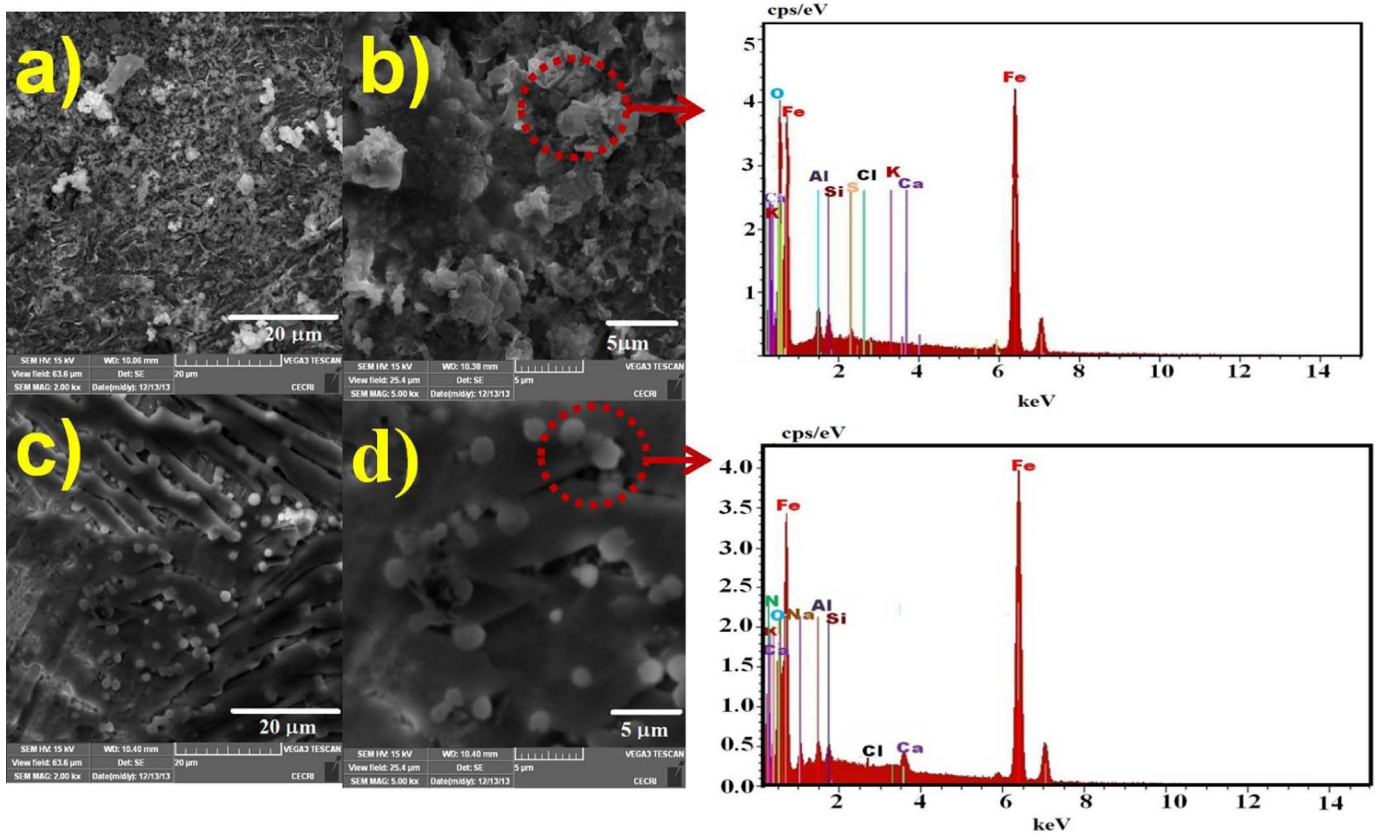


Fig. 8. SEM and EDAX images of steel specimen (a: 2k and b. 5k): Without EICI (c: 2k and d. 5k): With EICI.

C≡C move towards the cathode of embedded rebar and adsorbed on the metal surface. FTIR spectra confirm the presence of inhibitor on the rebar surface.

3.6.2. Scanning electron microscopy (SEM)

The scanning electron micrographs obtained for concrete samples before and after EICI treatment is shown in Fig. 7a and b respectively. SEM analysis indicated that the concrete sample before EICI shows highly porous in nature. On the other hand, the concrete samples after EICI treatment shows blocked pores. These observation proved that the hybrid inhibitor formulation act as pore blocking agent.

Scanning electron micrograph for steel specimen before and after EICI treatment is given in Fig. 8(a and b) and (c and d) respectively. It can be seen that unusual structure of iron chloride and iron oxide formation over the surface of steel. They are reaction products of Fe with chloride and oxygen/water. This was

further confirmed by the EDAX, which shows the presence of large % of chlorides.

Fig. 8(c and d) shows the micrograph for steel specimen after EICI treatment. Here it was clearly indicated a protective layer of inhibitors adsorbed on the steel surface. The EDAX results showed that the presence of the nitrogen group on the steel surface confirmed the fact that the injected solution reached the steel surface. The SEM and EDAX studies revealed that inhibitor adsorbed on the steel surface and also provide a sufficient protection to the steel from corrosion in the presence of chloride. SEM and EDAX results proved beyond doubt that the feasibility of EICI process in actual concrete and had a lot of scope to be implementing in field structures.

3.6.3. Mercury intrusion porosimetry

The data obtained for concrete samples before and after EICI treatment are shown in Fig. 9(a and b) respectively. From the data,

Elements	System	Fe	O	Cl	Ca	Si	Al	C	N
Weight (%)	Without EICI	54.09	14.58	10.93	12.06	3.73	3.64	0.38	---
	With EICI	67.84	14.25	0.25	11.23	1.62	1.87	0.91	1.82

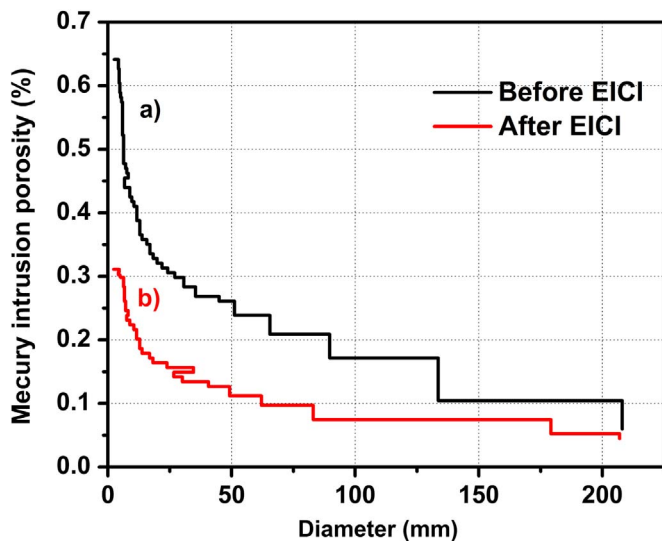
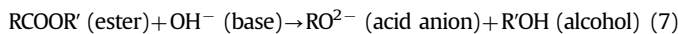


Fig. 9. Mercury intrusion porosity for before and after EICI treatment for concrete samples.

it was observed that nearly 50% reduction in porosity (0.6412 mm–0.3112 mm) for concrete samples after EICI treatment. These observations clearly confirmed the pore blocking effect of the inhibitor formulation.

3.6.4. Mechanistic action of EICI

The pore blocking effect by organic molecules in concrete is well established by ester - amine based inhibitors. The esters become hydrolysed by the alkaline mix water to form the carboxylic acid and its corresponding alcohol. The reaction proceeds as follows where R and R' represent different hydrocarbon molecules [23].



Actually in concrete, the carboxylic anion is quickly converted to the insoluble calcium salt of the fatty acid. Thus the fatty acids and their calcium salts formed provide a hydrophobic coating within the pores [24]. With the result, pore blocking effect of the inhibitor molecules is established.

The inhibited injection is a multi component system based on guanidine, thiosemicarbazide, triethanolamine and ethyl acetate. Each component in the inhibitor injection specified for a particular role in the process of electro injection and inhibition. For example, guanidine (CH_5N_3) is a crystalline compound of strong alkalinity and protonated as a guanidium cation $[\text{CH}_6\text{N}_3]^+$. The guanidinium cation has a charge of +1. It is a highly stable cation in aqueous solution due to the resonance stabilization of the charge and efficient solvation by water molecules. Hence its, pKa is 13.6 and act as a strong base in water. Similarly, thiosemicarbazide also protonated easily in aqueous solutions. Hence the protonated positive ions move towards the rebar. Ethyl acetate (ester) acts as a carrier for inhibiting ions. Additionally, amino alcohol ($\text{OH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$) rendering pore blocking property. As a whole, this multi component inhibited injection provides an effective adsorption on the steel surface and thereby provides a perfect passivating layer on the metal surface. Simultaneously the chloride anion present in the concrete move towards the anode.

The inhibition of the cathodic process is achieved by incorporation of one or more oxidizing anions in an organic (amine) molecule of inhibitors. The nitrogen atom of the amino group is capable of entering into a co-ordinate bond with metals, therefore enhancing the adsorption process. The adsorption of inhibitors

increases the over potential of metal ionization and slows down the corrosion process. The inhibitor's films serve as a buffer and maintain the pH level.

The inhibitor adsorption process is generally not instantaneous. It requires a defined time period for the successful formation of the adsorbed inhibitor layer on the target metal surface. There are two issues which need to be identified in order to ensure the successful adsorption:

- (1) The surface area in which the molecules occupy and
- (2) The necessary molecular binding energy

The inhibited injection was water soluble and possessed sufficient binding energy to metal surfaces that is higher than the binding energy of water dipoles. Also they create strong exothermic reactions which can displace surface water. This establishes an anchor point that prevents the corrosive species from reaching the metallic surface.

With the above reasons, the multi component hybrid inhibitor injection showed better efficiency in terms of reduction in corrosion rate in the presence of chloride.

4. Conclusions

Electro injection of organic corrosion inhibitors into the concrete revealed the following conclusions.

- Rebar potential measurements after EICI treatment indicated passive condition of the rebar even though the chloride content strongly reduced the passive film on steel surface.
- Potentiodynamic polarization technique proved that the EICI treatment is able to shift the rebar potential (+300 mV) towards passive region with the result the corrosion rate of rebar also reduced considerably.
- Electrochemical impedance studies indicated that systems after EICI showed a 5 fold increase in R_{ct} values when compared to system before EICI.
- Analysis of free chloride contents proved that the removal of chloride at the steel-concrete interfacial region is an added advantage during EICI treatment.
- FTIR studies indicated that the functional group of the inhibitors namely $-\text{NH}_2$, C–H and $\text{C}\equiv\text{C}$ move towards the cathode of embedded rebar and adsorbed on the metal surface and thereby provide inhibition.
- SEM analysis indicated that the hybrid inhibitor formulation act as pore blocking agent.
- MIP studies proved that nearly 50% reduction in porosity was observed for concrete samples after EICI.

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References

- [1] P. Ghods, O. Burkan Isgor, F. Bensebaa, D. Kingston, Angle-resolved XPS study of carbon steel passivity and chloride-induced depassivation in simulated concrete pore solution, *Corros. Sci.* 58 (2012) 159–167.
- [2] Tongyan Pan, Tuan Anh Nguyen, Xianming Shi, Assessment of electrical injection of corrosion inhibitor for corrosion protection of reinforced concrete, *J. Transp. Res Board* 2044 (2008) 51–60, <http://dx.doi.org/10.3141/2044-06>.

- [3] G.T. Parthiban, P. Thirumalai, R. Ravi, V. Saraswathy, N. Palaniswamy, V. Sivan, Cathodic protection of steel in concrete using magnesium alloy anode, *Corros. Sci.* 50 (12) (2008) 329–3335.
- [4] C. Christodoulou, G. Glass, J. Webb, S. Austin, C. Goodier, Assessing the long term benefits of impressed current cathodic protection, *Corros. Sci.* 52 (8) (2010) 2671–2679.
- [5] V. Saraswathy, Ha-Won Song, Improving the durability of concrete by using inhibitors, *Build Environ.* 42 (1) (2007) 464–472.
- [6] Saraswathy V, Ha-Won Song, Corrosion performance of rice husk ash blended concrete, *Constr. Build Mater.* 21 (8) (2007) 1779–1784.
- [7] S. Muralidharan, V. Saraswathy, S.P. Merlin Nima, N. Palaniswamy, Evaluation of a composite corrosion inhibiting admixtures and its performance in Portland pozzolana cement, *Mater. Chem. Phys.* 86 (3) (2004) 298–306.
- [8] R. Vedalakshmi, K. Rajagopal, N. Palaniswamy, Long-term corrosion performance of rebar embedded in blended cement concrete under macro cell corrosion condition, *Constr. Build Mater.* 22 (3) (2008) 186–199.
- [9] Ha-Won Song, V. Saraswathy, Analysis of corrosion resistance behavior of inhibitors in concrete using electrochemical techniques, *Met. Mater. Int.* 12 (4) (2006) 323–329.
- [10] B. Elsener, Corrosion Inhibitors for Steel in Concrete – State of the Art Report, European Federation Of Corrosion Publications, London, 2001.
- [11] C.L. Page, V.T. Ngala, M.M. Page, Corrosion inhibitors in concrete repair systems, *Mag. Concr. Res* 52 (1) (2000) 25–37.
- [12] T.A. Soylev, G.M. Richardson, Corrosion inhibitors for steel in concrete: State-of-the-art report, *Constr. Build Mater.* 22 (4) (2008) 609–622.
- [13] B.F. Johannesson, Diffusion of a mixture of cations and anions dissolved in water, *Cem. Concr. Res* 29 (8) (1999) 1261–1270.
- [14] Haibing Zheng, Li Weihua, M.A. Fubin, Qinglin Kong, The effect of a surface-applied corrosion inhibitor on the durability of concrete, *Constr. Build Mater.* 37 (2012) 36–40.
- [15] J. Tritthart, Transport of a surface-applied corrosion inhibitor in cement paste and concrete, *Cem. Concr. Res* 33 (6) (2003) 829–834.
- [16] T.A. Soylev, C. McNally, M.G. Richardson, The effect of a new generation surface-applied organic inhibitor on concrete properties, *Cem. Concr. Compos.* 29 (5) (2007) 357–364.
- [17] NACE-SP0107, Standard practice: electrochemical realkalization and chloride extraction for reinforced concrete. NACE International Houston, USA, 2007.
- [18] J. Bennett, K.F. Fong, T.J. Schue, Electrochemical chloride removal and protection of concrete bridge components, Field Trials, SHRP S-669, National Research Council, Washington DC, 1993.
- [19] S. Sawada, C.L. Page, M.M. Page, Electrochemical injection of organic corrosion inhibitors into concrete, *Corros. Sci.* 47 (88) (2005) 2063–2078.
- [20] G. Fajardo, A.G. Escadeillas, Electrochemical chloride extraction (ECE) from steel-reinforced concrete specimens contaminated by artificial sea-water, *Corros. Sci.* 48 (1) (2006) 110–125.
- [21] S. Sawada, J. Kubo, C.L. Page, M.M. Page, Electrochemical injection of organic corrosion inhibitors into carbonated cementitious materials: Part 1. Effects on pore solution chemistry, *Corros. Sci.* 49 (3) (2007) 1186–1204.
- [22] S. Muralidharan, R. Vedalakshmi, Saraswathy V, James Joseph, N. Palaniswamy, Studies on the aspects of chloride ion determination in different types of concrete under macro-cell corrosion conditions, *Build. Environ.* 40 (9) (2005) 1275–1281.
- [23] F.A. Carey, R.J. Sundberg, *Advanced Organic Chemistry, Part A: Structure and Mechanisms*, second ed., Plenum Press, New York, 1981.
- [24] C.K. Nmai, Multifunctional organic corrosion inhibitor, *Cem. Concr. Compos.* 26 (3) (2004) 199–207.