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Electrochemical Protection of Steel in Concrete to Enhance the Service Life of Concrete Structures

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Abstract

Corrosion of steel in concrete is a major threat to the construction industry. Ingress of chloride is the main cause of reinforcement corrosion. To prevent corrosion many protection methods are adopted viz, coating to concrete, coating to rebar, adding inhibitors, using supplementary cementations materials and electrochemical protection of steel, etc., Electrochemical protection of steel is one of the method adopted to protect and minimize the rebar corrosion both for existing and new concrete structures. In the present investigation an inhibitor injection was formulated to mitigate reinforcement corrosion in chloride contaminated concrete. In the first stage, the efficiency of the inhibitor injection was tested in different cement environments. In the second stage, the inhibitor formulation was injected into Ordinary Portland Cement (OPC) and Portland Slag Cement (PSC) with different concentrations of chloride. The efficiency of the electro injection process was evaluated by electrochemical techniques. Electrochemical measurements show that the EI process has a high inhibition efficiency than migration process. Electro injection process showed a remarkable decrease in the corrosion rate of embedded in concrete steel even in the presence of aggressive chloride ions when compared to systems without electro injection. In the third, the long term performance of the effectiveness of the electro injection process was studied in concrete slab for an exposure period of 3 months. EI process not only enhanced the inhibition property but also removes the free chloride ions from the chloride contaminated concrete. FT-IR results confirmed that the inhibitor formulation has formed a passive layer on the surface of the steel rebar even in the presence of chloride through the electro injection process.

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Keywords: Reinforcement corrosion; Electro injection; inhibited injection solution; passivity

1. Introduction

Corrosion of steel in concrete is a worldwide problem. It is influenced by various factors such as carbonation, chloride ingress, etc., One of the early deterioration mechanisms is chloride-induced steel corrosion in concrete. Among them chloride ingress plays an important role in decreasing the durability of concrete structures.

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Several researchers protected the steel in concrete by various methods such as coatings to steel, coatings to concrete, cathodic protection (CP), addition of super plasticizers, electrochemical removal of chloride, desalination, electrochemical re-alkalization and corrosion inhibiting admixtures have been reported [1-7]. The method of partial replacement is considered the conventional option, for repair and rehabilitation but it can be time-consuming, expensive and inconvenient, often associated with noise, dust and general disruption during the repair process. As far as electrochemical re-alkalization is concerned, criteria for determining completion of a successful treatment and its long-term durability have been somewhat unclear [8] and, desalination is the established method used for extracting chloride ions from concrete [9,10]. This technique has an advantage of being a fast and temporary treatment, although chloride ions cannot be completely removed in the treatment [11,12]. Therefore, it is important to improve the chloride removal and simultaneously protect the steel by electro injection techniques. Two organic migrating inhibitors (amine- and alkanolamine based) were applied on the surface of concrete and the results showed that migrating inhibitors were not effective in reducing the corrosion rate, either for chloride or carbonation induced corrosion, although some effect was observed on delaying the initiation of corrosion in the case of chloride penetration. The effectiveness of the inhibitors was evaluated by long-term rebar corrosion monitoring in reinforced concrete, and by visual inspection of rebars after five years of testing. The results provide useful information on the corrosion prevention ability of the inhibitors, both on time-to-corrosion and on corrosion propagation.

The objective of the present investigation is directed towards the evaluation of a designed multi component inhibitor injection solution consists of thiosemicarbazide, tri-ethanolamine, guanidine and ethyl acetate were used as electrolyte formulation for the corrosion of steel in different types of concrete (OPC, PPC & PSC) with varying chloride levels through the electro injection process. In the first stage, the efficiency of the inhibitor formulation is tested in the different cement extract medium. Long term performance of the electro injection process is also monitored for an exposure period of 12 months.

2. Materials and Methods

2.1. Materials

The various types of cement namely ordinary Portland cement (OPC) (IS: 8119-1989), Portland pozzolana cement (PPC) (IS: 1489 (part-1) 1991- fly ash based and Portland slag cement (PSC) (IS: 455-1989) were used. The chemical composition of OPC, PPC and PSC is given in Table 1. Local clean river sand (fineness modulus of medium sand equal to 2.6) conforming to grading zone-III of IS: 383–1970 was used. The specific gravity of fine aggregates is 2.4. Water absorption of fine aggregates is 0.5%. All the solutions were prepared using distilled water. Inhibited injection solution consists of 0.1M guanidine, 0.1M thiosemicarbazide; 2M triethanolamine and 2M ethyl acetate. Sodium chloride (3%) by weight of cement was added to the concrete during casting. Thermomechanically treated (TMT) rebar of size 12 mm diameters was used. The composition of PC-TMT (wt. %) are as follows: C=0.17; Mn=0.88; P=0.023; Si=0.075; S=0.038 and Fe remainder with carbon equivalent= 0.32%.

Constituent	Wt(%)		
	OPC	PPC	PSC
SiO_2	20-21	28-32	26-30
Al_2O_3	5.2-5.6	5.0-8.0	9.0-11.0
Fe_2O_3	4.4-4.8	4.9-6.0	2.5-3.0
CaO	62-63	43-45	44-46
MgO	0.5-0.7	1.0-2.0	3.5-4.0
SO_3	2.4-2.8	2.4-2.8	2.0-2.4
LOI	1.5-2.5	3.0-3.5	1.5-2.5

Table 1: Chemical composition of OPC, PPC and PSC cements

2.1.1. Casting of Reinforced Concrete Cube

A cubical concrete specimen of size 100 mm X 100 mm X 100 mm and concrete slab specimen of size 1 m X 1 m X 0.1 m were cast using OPC, PPC and PSC with 3% NaCl by weight of cement. The rebar size is 12 mm diameter and 950 mm length, were embedded with a concrete cover thickness of 25 mm. Concrete specimens were cast using 1:1.8:3.69 mix (cement: 369.79 kg/m^3; sand: 665.63 kg/m^3; coarse aggregates: 1364.52 kg/m^3 and NaCl: 11.09 kg/m^3 (3% NaCl by weight of cement) with a w/c ratio of 0.55. During casting, the specimens were mechanically vibrated. After 24 hrs, the specimens were demoulded and cured for 28 days in distilled water to avoid any contamination. Both concrete specimens were given enough time to induce accelerated corrosion of steel rebar due to aggressive chloride ion.

2.2 Electro Injection Process

Cube: Concrete specimen is placed in an electrolytic cell immersed with inhibited injection solution. Rebar embedded in concrete acts as cathode and stainless steel plate act as anode. The electrolytic cell was galvanostatically maintained at a D.C current density of 0.5 A m^{-2}.

The following parameters were monitored on electro injected specimens.

2.2.1. Open Circuit Potential (OCP)

OCP measurements were carried out regularly for the rebar embedded in concrete as per ASTM C-876.

2.2.2. Potentiodynamic Polarization Studies

After the electro injection process, the same setup was made use of polarization measurements to carry out in order to evaluate the corrosion kinetic parameters. Both cathodic and anodic polarization curves were recorded potentiodynamically using ACM Instruments, UK.

2.2.3. A.C. Impedance Measurements

After the electro injection process, TMT steel rebars embedded in concrete specimens were subjected to A.C impedance measurements. The same three electrode cell assembly was used here also. The real part (Z′) and the imaginary part (−Z″) of the cell impedance were measured for various frequencies (30000–0.01 Hz). Plots of Z′ versus −Z″ were made. For comparison, impedance was also carried out for the system without electro injection.

2.2.4. Estimation of Various Chloride Contents

At the end of an electro injection process, the amount of chloride released into the electrolyte was estimated. The amount of residual free chloride and bound chloride contents in concrete was also estimated as per the standard procedure [13].

3. Results and Discussion

3.1. Evaluation Electro Injection Process into the Concrete

3.1.1 Potential-time Behaviour

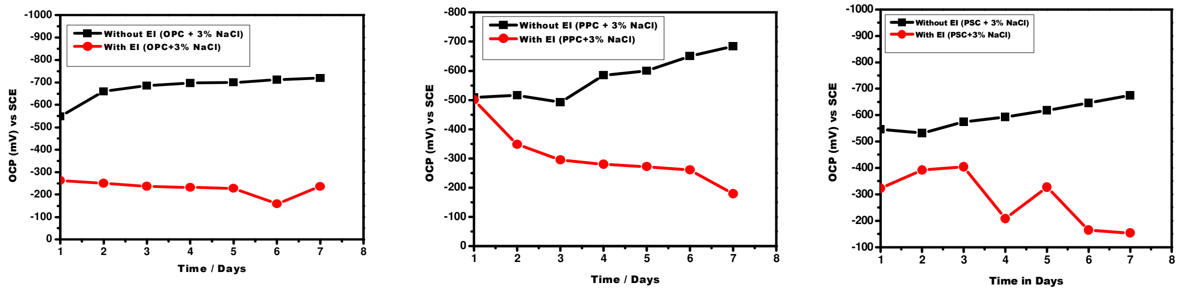
The OCP of embedded steel in different concrete system was noted during the electro injection process is given in Fig.1a. Here it was observed that inhibited injection system shifted the potential towards a more positive direction when compared to a system without injection. At the end of 7 days, the OCP of TMT steel was found to be -719 mV for system without electro injection and -236 mV for systems with electro injection. This observation clearly brings out the fact that inhibitor injection is able to inject electrochemically into the concrete and reached the steel and shifted the potential towards a more positive direction and protect the rebars from the corrosive environments. The inhibition of corrosion was due to the passivation of steel surface by inhibitors.

Similarly PPC concrete admixed with 3% NaCl during the electro injection process is given in Fig.1b. As observed in the OPC concrete, here also electro injection was found effective and shifted the potential towards the positive side. The difference in the shifting of potential for systems with and without electro injection process was as high as 505 mV for 3 % chloride. These data confirmed that the inhibitor molecules reached the steel surface and maintained the steel in passive condition.

The potential-time behaviour of TMT steel embedded in PSC concrete admixed with 3% NaCl during the electro injection process is given in Fig.1c. As observed in the OPC and PPC concretes, here also electro injection was found effective and shifted the potential towards the more positive side. At the end of electro injection the potential for various systems are as follows:

Without electro injection: - 675 mV vs. SCE
With electro injection: -154 mV

Potential-time studies indicated that a multi component inhibitor injection was quite suitable for electro injection process into concrete even in the presence of higher amount of chloride ions. The whole process was successfully completed within 7 days which is quite reasonable time for the repair and rehabilitation of any concrete structures. Among the three types of concrete studied, PSC performed well in all the three chloride levels.



(a) (b) (c)

Fig.1. Potential–time behaviour for rebar embedded in (a).OPC , (b).PPC and (c).PSC concretes during electro injection (EI) process

3.1.2. Estimation of Released Free Chloride Contents

Table 2. Shows the amount of free chloride released into the electrolyte with respect to different systems at the end of the electro injection process. It was observed from the table that a considerable amount of free chloride is released into the electrolyte for all the systems at the end of 7 days. During electro injection process 2410 ppm, 2148 ppm and 2143 ppm of free chloride is estimated in the electrolyte within 7 days of exposure for OPC, PPC and PSC concretes respectively. The release of free chloride from concrete is an added advantage of the electro injection process. Compared to OPC concrete, blended concrete (PPC and PSC) released less free chloride contents into the electrolyte. This is due to the fact that chloride binding capacity of Portland pozzolona and Portland slag concrete is greater than Portland cement concrete. Therefore it favors the formation of more complex Friedel's salt [$3CaO.Al_2O_3.CaCl_2.10H_2O$] [14]. Hence the the formation of bound chloride was maximum for PPC (3955 ppm) and PSC (4005 ppm) than OPC (3568 ppm).

3.1.3. Potentiodynamic Polarization Studies

The typical polarization curves for TMT steel embedded in OPC, PPC and PSC concretes admixed with 3% NaCl after electro injection is shown in Figs 2 to 4. Polarization curves obtained for TMT steel embedded in concrete admixed with 3% NaCl without electro injection is also given in the above figures for comparison.

The corresponding corrosion kinetic parameters are given in Table 3.

Here it was observed that systems with electro injection showed less i_{corr} values than systems without electro injection. The corrosion rate for TMT steel in OPC concrete with and without electro injection was found to be 0.6993 mmpy and 10.6500 mmpy respectively. A similar observation was noticed in PPC and PSC systems studied. 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 TMT steel in concrete. The efficiency of the electro injection process calculated on the basis of reduction in corrosion rate was found to be >93% in all the systems studied.

It is a fact that the electrochemical behavior of steel in concrete is expected to be in passive, although is very well known that in the presence of chlorides the passive range is reduced (pitting potential vs. transpassivity). Only when very high chloride concentration of chlorides is present the behaviour becomes active. These observation was noticed from Figs 2 to 4 that, the specimen without electroinjection which contains high concentration of chloride shows only active condition of rebar. On the other hand, specimens with electroinjection shows a passive condition of rebar. The exchange current density values are also shifted from 10^{-3} mA.cm^{-2} to 10^{-5} mA.cm^{-2}. All these results confirmed that electoinjetcion process was effective and protect the steel by passivation mechanism.

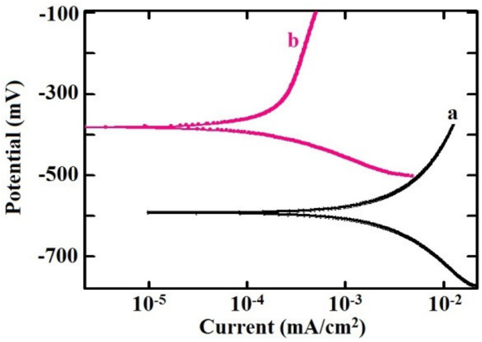


Fig.2. Potentiodynamic polarization curves for rebar embedded in OPC(OPC+3% NaCl) concrete after electro injection process
(a).Without electro injection
(b).With electro injection

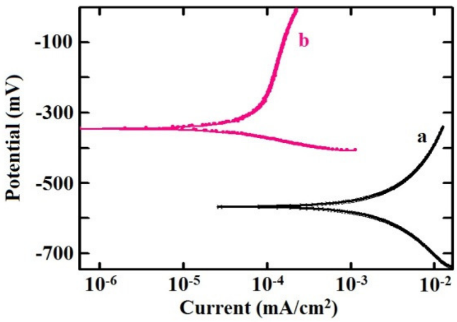


Fig.3. Potentiodynamic polarization curves for rebar embedded in PPC(PPC+3%NaCl) concrete after electro injection process
(a) Without electroinjection
(b) With electroinjection

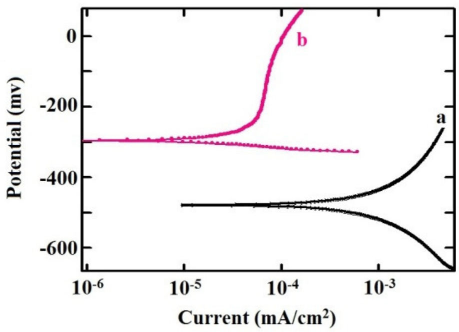


Fig.4. Potentiodynamic polarization curves for rebar embedded in PSC(PSC+3% NaCl) concrete after electro injection process
(a).Without electro injection;
(b) .With electro injection

3.1.4. Impedance studies

The typical Nyqusit plots for TMT rebar embedded in electro injected concrete are shown in Figs.5 to 7. Impedance plots for TMT steel embedded in concrete admixed with 3% NaCl without electro injection is also given in the above figures just for comparison. The impedance parameters are given in Table 4. Here it was observed that almost all the Nyquist plots are not perfect semi circles and this may be due to frequency dispersion. It is interesting to note that systems with electro injection showed a 5 times increase in R_{ct} values when compared to systems without electro injection. For example OPC concrete showed R_{ct} values of 1.019 x10^4 Ω.cm^2 and 5.735x10^4 Ω.cm^2 for systems without electro injection and with electro injection respectively. Similar trend in R_{ct} values were noticed for PPC and PSC concretes also. Electro injected specimens showed lower magnitude of corrosion current (i_{corr}) when compared to without electro injected specimens. The same observation was already noticed in potentiodynamic polarization studies also.

System	Cement	Various chloride contents			
		Amount of chloride added before EI (ppm)	Chloride Released during EI(ppm)	Residual free chloride in concrete after EI (ppm)	Residual bound chloride in concrete after EI(ppm)
Without electroinjection	OPC	6600	---	3523	3568
	PPC	6600	---	3147	3877
	PSC	6600	---	3067	3989
With electro injection	OPC	6600	2410	1085	3568
	PPC	6600	2148	921	3955
	PSC	6600	2143	898	4005

Table 2 : Amount of various chloride contents in concrete before and after electro injection (EI) process

System	Cement	E_{corr} (mV vs. SCE)	I_{corr} (mA.cm^{-2}) X 10^{-5}	Corrosion rate (mmpy) X 10^{-3}	Inhibitor efficiency (%)
Without electroinjection	OPC	-591	91.910	10.650	--
	PPC	-567	82.080	9.512	--
	PSC	-478	30.690	3.556	--
With electroinjection	OPC	-282	6.034	0.699	93.43
	PPC	-345	2.276	0.263	97.22
	PSC	-295	2.024	0.234	93.40

Table 3 : Polarization parameters for the corrosion of rebar embedded in OPC, PPC and PSC concretes with and without electro injection process

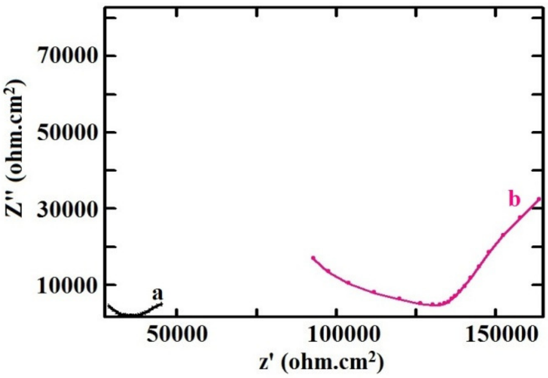


Fig.5. Impedance plots for TMT steel in OPC (OPC+3%NaCl) after electroinjection process
(a) Without electro injection
(b) With electro injection

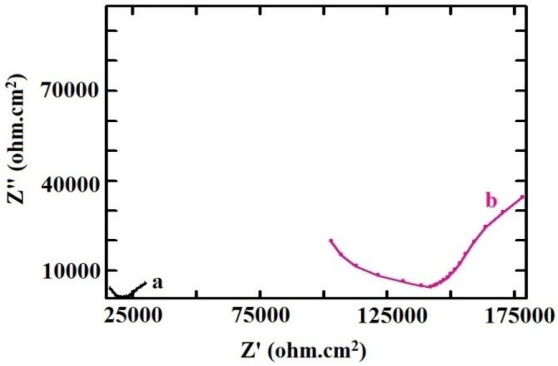


Fig.6. Impedance plots for TMT steel in PPC(PPC+3%NaCl) after electroinjecti -on process (a) Without electroinjection
(b) With electroinjection

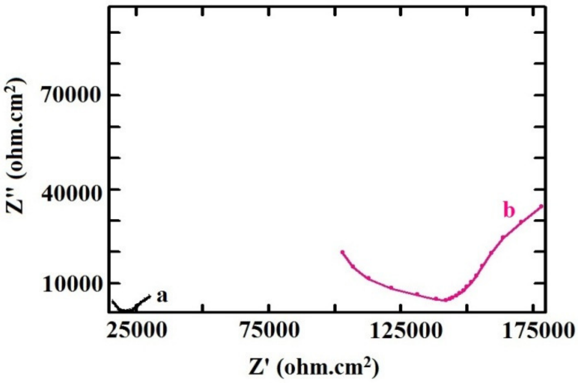


Fig.7. Impedance plots for TMT steel in PSC(PSC+3% NaCl) concrete after electro injection process (a).Without electro injection; (b).With electro injection

System	Cement	Impedance parameters		
		I_{corr} (mA.cm^{-2}) X 10^{-3}	Corrosion rate (mmpy) X 10^{-2}	R_{ct} Ω.cm^2 X 10^4
Without electroinjection	OPC	2.560	2.969	1.019
	PPC	2.520	2.921	1.035
	PSC	2.311	2.678	1.124
With electro injection	OPC	0.4549	0.527	5.735
	PPC	0.4527	0.524	5.762
	PSC	0.4157	0.481	6.275

Table 4 : Impedance parameters for the corrosion of rebar embedded in OPC, PPC and PSC concretes with and without electro injection process

4. Conclusions

The following can be drawn from the present investigations:

- A new inhibited injection is designed and successfully injected into concrete at a cathodic current density of 0.5 Am^{-2}.
- Potential- time studies indicated that within 7 days of exposure, the rebar potential shifted towards more positive direction even in the presence of chloride.
- The release of free chloride contents from concrete is an added advantage of electro injection process. Blended concrete released less free chloride contents.
- Potentiodynamic polarization studies proved that the corrosion rate of embedded steel was drastically reduced for systems with electro injection. The multi component inhibitor injection showed more than 95% efficiency in terms of reduction in corrosion rate irrespective of chloride levels in different concretes.
- Electro injection showed a 2 times increase in R_{ct} values when compared to systems without electro injection.

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