



**HYBRID INHIBITORS FOR REINFORCED CONCRETE – A NOVEL
ELECTROCHEMICAL APPROACH FOR CHLORIDE REMOVAL**

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Abstract: *The Inhibiting effect of a novel multi component inhibitor formulation was studied under electro injection (EI) and migrating conditions using Ordinary Portland Cement (OPC) and Portland Slag Cement (PSC) with different concentrations of chloride. Electrochemical measurements show that the EI process has high inhibiting efficiency than migration process. EI process not only enhanced the inhibiting 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 higher chloride through electro injection process.*

Keywords: *inhibitor formulation, migrating, E-injection, chloride contaminated concrete, passive layer*

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1. INTRODUCTION

Corrosion of steel in concrete is influenced by various factors such as pH reduction, carbonation, chloride ingress etc. among them chloride ingress play a vital role in decreasing the durability of concrete structures. To counteract this problem, various preventive measures such as coating of steel, coating of concrete, cathodic protection, addition of super plasticisers and corrosion inhibiting admixtures have been reported [1-5]. Corrosion inhibitors are considered as one of the most cost-effective solutions. The use of corrosion inhibitors is wide spread and well established. Different types of inhibitors are available today, but in many cases the mechanism of inhibitor is not fully understood [6]. Earlier studies of corrosion inhibitors focused on sodium benzoate, various nitrites and chromates/dichromates [7-10] as concrete admixtures to inhibit corrosion in reinforced concrete. During 1990s a number of organic inhibitors were developed. Several nitrogen and sulphur containing compounds, amino alcohol based [11-13], thiosemicarbazide [14] and carboxylate based corrosion inhibitors were investigated. Amino alcohol and carboxylate based corrosion inhibitors show dual actions in concrete as the amine compound acts as inhibitors, whereas the carboxylate ester compound has pore blocking effect [15-19]. Calcium nitrite has been used as corrosion inhibitor to reduce corrosion rate in non-carbonated concrete with chloride contamination [20-21]. Muralidharan et.al reported that citrate and stannate-based inhibitors showed good performance in OPC and fly ash extracts [22]. Gadadhar and Balasubramaniam have investigated the behaviour of phosphoric irons in simulated concrete pore solution, and they reported that phosphoric irons can be used advantageously in concrete environment as corrosion resistant reinforcement materials [23]. ZnO has been used as a corrosion inhibitor for long term performance, the use of ZnO reduces the concrete porosity and chloride content level [24]. Sawada et al., have studied the electrochemical injection of organic corrosion inhibitors based on alkanol amine and Guanidine [25].

In the present investigation, the inhibiting effect of a multicomponent inhibitor was studied under Electro Injection (EI) and Migration process (MI) under chloride contaminated reinforced OPC and PSC.



2. EXPERIMENTAL PROCEDURE

2.1. Materials used

Ordinary Portland cement (OPC) (IS: 8119-1989) and Portland slag cement (PSC) (IS: 455-1989) was used throughout this investigation. The chemical composition of OPC and PSC was given in Table 1. The different systems studied were given in Table 2.

2.1.1 Preparation of cement extracts

Cement was sieved through 90 μm sieve and extracts were prepared as follows. To 100 g of the cement, 100 ml of distilled water was added and shaken vigorously using a Microid flask mechanical shaker for about 1 h. The extracts were then collected by filtration and the pH was measured using pH meter. The pH of OPC and PSC extracts was 12.76 and 12.54 respectively. The initial chloride level for the various extracts was found to be 20 to 25 ppm.

2.2. Inhibitor formulation

The inhibitor formulation consists of 0.25M Pyrollidine, 0.05M Glutamine, 0.25M Ethyl Acetate and 0.25M Sodium Nitrite was used for the investigation.

METHODS

2.3. Application of Inhibitor formulation into concrete

2.3.1. Casting of concrete specimens

Cylindrical concrete specimen of size 55 mm diameter and 60 mm height were cast using OPC and PSC with varying percentages of sodium chloride ranging from 1% to 3% on the basis of weight of cement. Steel rebar of 12 mm dia and 50 mm long, were embedded in the center of each specimen. Concrete specimens were cast using 1:1.8:3.69 mix with w/c 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.

2.3.2. Electro injection (EI) process

250 ml of electrolyte (Hybrid inhibitor formulation) was taken in the electrolytic cell with TMT rebar embedded in concrete specimen and perforated cylindrical stainless steel plate acts as cathode and anode respectively. A current density of 1 A/m^2 was galvanostatically maintained over an exposure period of 7 days.



2.3.3. Migrating Inhibitor (MI) process

In this process, inhibitor was applied on the external concrete surface either by brushing or by spraying. This process was repeated for 3 times at a time-interval of 24 hours. Sufficient amount of inhibitors required for inhibiting action was achieved in 15 days.

2.4. pH measurements

The pH of the extract was measured using a portable Istek Inc. (Model 76 P) pH meter. The pH meter was calibrated using buffer solution of pH 9. Minimum of 3 readings was noted for each system and average pH value was reported. pH values were measured initially and also at the end of the exposure period.

2.5. Electrochemical techniques

2.5.1. Potentiodynamic polarization technique

Potentiodynamic polarization studies have been carried out using three electrode cell assembly. Embedded rebar in concrete acts as working electrode, Saturated Calomel Electrode (SCE) and the Stainless Steel (SS) as reference and counter electrodes respectively. Both anodic and cathodic polarization curves were recorded potentiodynamically using ACM instrument, UK. This instrument itself is having provisions for programs to evaluate corrosion kinetic parameters such as I_{corr} , E_{corr} , b_a and b_c . The potentiodynamic condition corresponds to a potential sweep rate of 60 mV/minute and potential ranges of -200 to +200 mV from the open circuit potential (OCP). All the experiments were carried out at a room temperature of $35 \pm 1^\circ\text{C}$.

2.5.2. Electrochemical Impedance Spectroscopy (EIS)

The same three-electrode cell assembly was used for carrying out EIS. A time interval of 10 to 15 minutes was given for the OCP to reach a steady state value. The impedance measurements were carried out using ACM Instruments, UK. The real part (Z') and imaginary part ($-Z''$) of the cell impedance were measured for various frequencies (30 kHz to 10 mHz). Plots Z' Vs. $-Z''$ were made. Impedance measurements were carried out for migrating and electro injected specimens.

2.6. Visual observations

After split open the concrete, rebar specimens were taken out and carefully examined for any corrosion products like red rust, pits observed on the surface of the rebar with magnifying lens.



2.7. Weight loss measurements

TMT steel rebar of size 12 mm dia and 70 mm height were subjected to cleaning in the pickling solution as per ASTM-G1-90. After pickling, the rebar specimens were washed with water, dried and the initial weight of the rebars was measured. The rebars were embedded into the cylindrical concrete specimens which contain 0-3% chlorides admixed for inducing the corrosion, the specimen were immersed in water for curing in 28 days. After curing, the specimens were ready for migrating and electro-injection process. The weight loss measurements were conducted on the sample at the end of the exposure period. The specimens were broken and the embedded steel rebar specimens were subjected to cleaning in the pickling solution. After cleaning, the rebars were washed with water, dried and the final weight of the rebars was measured. The specimens were reweighed and the loss in weight was calculated. From the weight loss values, the corrosion rates were obtained from the following relationship.

$$\text{Corrosion rate} = \frac{87.6W}{DAT}$$

Where, W is the weight loss in milligram, D is the density of the material used (g/cm^3), T is the time duration in hours, A is the area of the specimen (cm^2).

2.8. FT-IR Spectroscopy

The concrete specimens were broken and the powder sample collected very near to the surface of the rebar were subjected to FT-IR studies using MAKE-BRUKER Optik GmbH FT-IR spectrometer (Model No-TENSOR27)

3. RESULTS AND DISCUSSION

3.1. PH measurements

PH values measured for plain, MI, and EI were given in Table 2. From the Table it was found that the pH was not affected by the addition of inhibitors. Presence of chloride also has no effect on the alkalinity.

3.2. Potentiodynamic polarisation technique

The data collected from potentiodynamic polarization studies were given in Table 3. The results obtained revealed that, all the MI and EI systems have shown higher LPR values when compared to the control system. Icorr values were found to be very less for MI systems when compared to control but it is greater than EI system indicating the better



performance. Among all EI, PSC shows lower corrosion rate of 0.0005 mmpy than OPC of 0.0069 mmpy at 3 % chloride concentration. The inhibition efficiency for EI was found to be a minimum of 91.11% to a maximum of 95.83%. Even at higher chloride concentration the inhibition efficiency was found to be greater than 90%, which shows the hybrid inhibitor has a synergistic effect which enhanced the efficiency. In EI, the hybrid inhibitor retards the corrosion mechanism by controlling cathodic reactions predominantly and blocking cathodic area of the steel rebar. The I_{corr} value increases with increasing the Cl^- ion concentration. I_{corr} and LPR values confirmed that EI shows good inhibiting efficiency against corrosion. From Figs.1-2, it was confirmed that the potential shifted towards the passive region for EI system.

3.3. Electrochemical Impedance Spectroscopy

Table 4 and Figs.3, 4 depict the EIS results. From the results it was observed that R_{ct} value was found to be higher for the control system when compared to MI and EI systems. Steel embedded in control system indicated a corrosion rate of 0.0758 mmpy in OPC and 0.0730 mmpy in PSC concrete respectively at 3 % chloride concentrations. Whereas OPC and PSC have shown corrosion rate of 0.0395, 0.0137 and 0.0176, 0.0091 mmpy for MI and EI treated systems respectively at 3% Cl^- concentration. In general, a high resistance with lower capacitance value is expected for a good system. Interestingly MI and EI systems have shown lesser capacitance value than the control system [26]. The inhibiting efficiency was found to be higher for EI system showing the better performance. When compared to OPC and PSC in EI, PSC was found to perform better than OPC which is well evidenced from this EIS study.

3.4. Weight loss measurements

The weight loss measurements of TMT steel was given in Table 5. It was observed that the corrosion rate was found to be 0.2035 mmpy and 0.2166 mmpy at 3% Cl^- for control systems of OPC and PSC respectively. System which is showing corrosion rate lesser than 0.2035mmpy and 0.2166mmpy were considered to be the best system. From the Table, both EI and MI systems have shown lesser corrosion rate and good inhibiting efficiency at all Cl^- concentrations. These results agreed with the corrosion rate measured using potentiodynamic polarization and EIS studies. The overall trend of corrosion rate obtained from various experiments of the hybrid inhibitor was expressed as Control > MI >EI.



3.5. Visual Observations

Table 6 shows the comparison of rusting area percentage by visual examination; at the end of an exposure period. The percentage of rusting area was reduced about 50% even at higher chloride concentration due to the formation of passive layer on the surface of the rebar. Among all, EI showed 3 times better protection against corrosion at 3% chloride concentration.

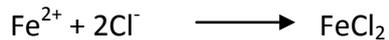
3.6. Surface Coverage versus concentration of Cl⁻ ions

Fig.5 shows the adsorption isotherm studies of the hybrid inhibitor at different chloride concentrations. From the Figure it was confirmed that the hybrid inhibitor obeys Temkin adsorption isotherm. The surface coverage decreases with increase in concentration of chloride ion in all the systems studied [31]. In EI, the inhibiting efficiency was found to be more than 90% irrespective of the chloride concentration which confirms the passive layer formation due to the chemisorption of the inhibiting ions on the surface of the rebar through chemical bonding. MI also exhibits the same behaviour but the inhibiting efficiency varied from 57% - 96% for all the systems studied.

3.7. FT-IR spectroscopy

The EI concrete specimens were broken and the surface of the embedded steel was subjected to infrared spectral analysis and was given in Fig.6 & Fig.7. The observed peaks confirmed that there is a formation of passive layer on the surface of the steel embedded in concrete and the peaks were observed due to the stretching vibration of the following groups. The broad peak at 3700 to 3600 cm⁻¹ is corresponding to the OH stretching vibration. The peak at 3400 and 3300 cm⁻¹ is corresponding to -N-H stretching vibration. The peak at 1650 and 1550 cm⁻¹ is corresponding to -N-H bending vibration in amines. The peak at 800 and 600 cm⁻¹ is corresponding to Fe-Cl stretching vibration [27]. IR spectral result confirmed that the novel inhibitor formulation can able to migrate through concrete and form a passive layer on the surface of embedded steel even in the presence of chloride through electro injection process.

The spectrum obtained by stretching vibrations illustrate that the formation of passive layer due to charge transfer transition of the ligand (-NH₂) to the vacant d-orbital of the metal (Fe²⁺). This ligand-metal charge transition (LMCT) proposed the following mechanism [28].



3.7. Role of inhibitor formulation in corrosion resistant properties of TMT steel

The inhibitor investigated in the present research is an amine and ester based organic inhibitor. The main component is amine based alcohol, which is the volatile component and is transported mainly by diffusion process. The second component is in general an acid component. This acid component is reported to react with hydration products. The reaction with calcium hydroxide results in a gel formation that blocks the pores of the concrete. For amine - ester based inhibitors; the pore-blocking effect is suggested as a secondary property as it causes a reduction in the chloride ingress into concrete. This pore blocking effect is likely to change some other concrete properties (rather than only the permeability) as the porosity system in concrete affects most of the properties. The inhibitor formulation is a hybrid system based on aminocarboxylate compound. Each component in the inhibitor formulation specified for a particular role in the process of inhibition, such as aminocarboxylate rendering pore blocking effect [15-19], amines for inhibition and adsorption [29], $-\text{NO}_2$ for passivation [30-31] and ester for film formation [32]. These water-insoluble organic compounds that contain a medium-length hydrocarbon chain with a polar group at one end are found to spread on the surface spontaneously to give a surface film through the inhibiting ions from the solution into the metal surface.

CONCLUSIONS

The following conclusions can be drawn from the above investigation,

- The hybrid inhibitor formulation has good inhibiting efficiency even at 3% Cl^- contaminated OPC and PSC concrete. Hence, this inhibitor is well suited for marine environment.
- MI, EI treated OPC and PSC gives better performance as compared to control. The corrosion rate was observed from various experiments illustrated as follows, Control > MI > EI.
- Surface coverage obtained from weight loss measurements and visual observations shows that passive layer formation takes place on steel surface due to chemisorption of inhibiting ions. Adsorption isotherm studies confirmed that hybrid inhibitors obeys Temkin adsorption isotherm.



- The passive layer formed by hybrid inhibitor due to charge transition was confirmed by FT-IR spectroscopy.
- Potentiodynamic polarization studies and EIS confirmed that EI treated TMT steel of PSC shows higher inhibiting efficiency and lower corrosion rate than OPC even at higher Cl^- concentration.
- This investigation confirms that EI was an excellent tool to apply inhibitor through concrete. In EI process the inhibiting efficiency of the steel as well as Cl^- removal from the concrete takes place simultaneously. Hence, corrosion rate was reduced. Because of the dual purpose, EI can be used for repair and rehabilitation of damaged concrete structures effectively.

ACKNOWLEDGEMENTS:

The authors would like to thank CSIR-IHEAL project for providing the financial support.

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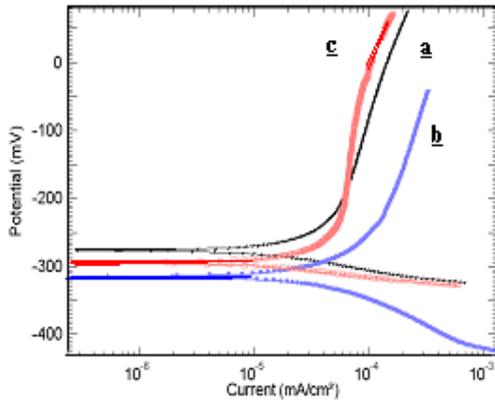


Fig.1a:

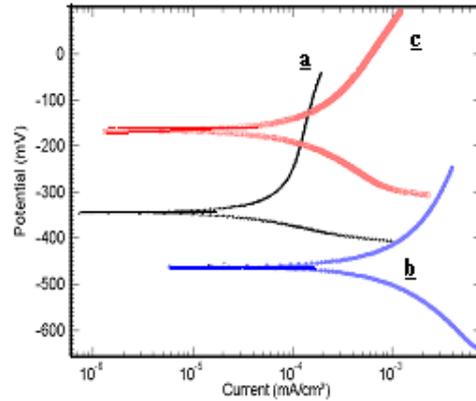


Fig.1b:

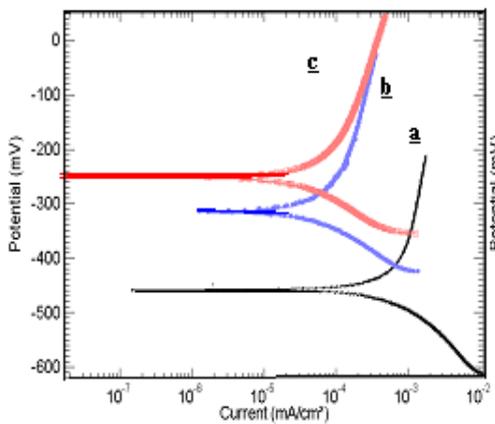


Fig.1c: OPC+2%Cl⁻

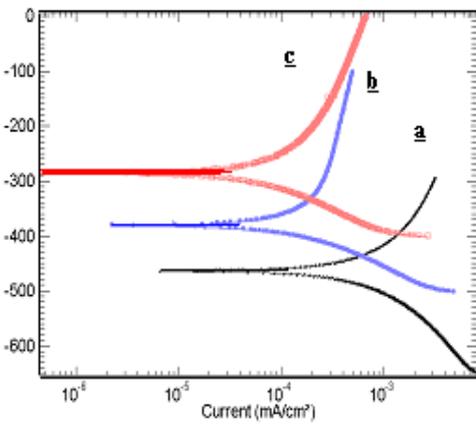


Fig.1d:

Fig.1. Tafel polarization curves of TMT steel embedded in OPC concrete admixed with various levels of chloride

a - control, b - Migrating (MI), c - Electro injection (EI),

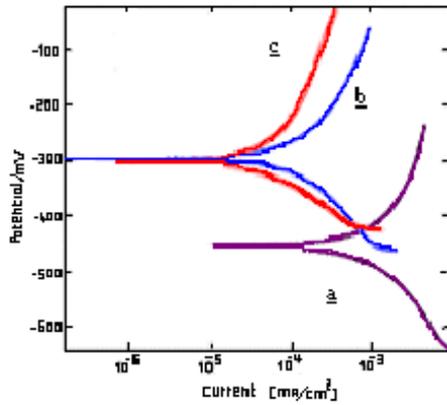


Fig.2a:

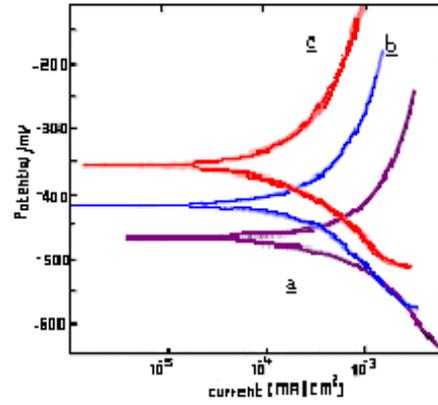


Fig.2b:

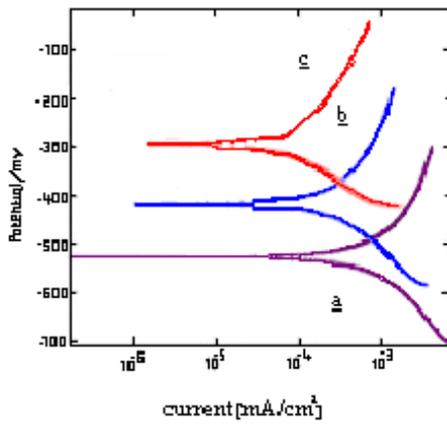


Fig.2c:

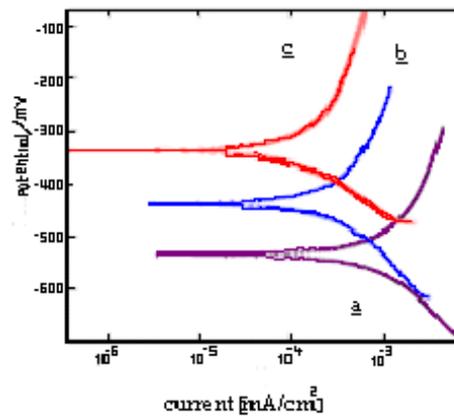


Fig. 2d:

Fig.2. Tafel polarization curves of TMT steel embedded in PSC concrete admixed with various levels of chloride

a - control, b - Migrating (MI), c - Electro injection (EI),

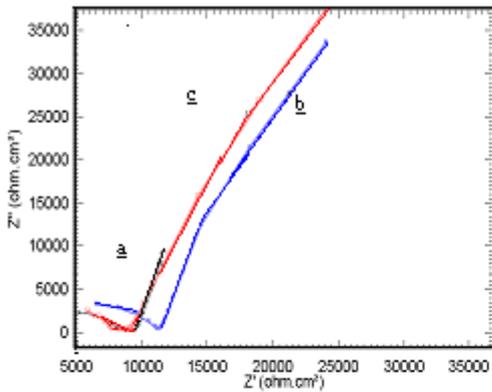


Fig.3a:
OPC

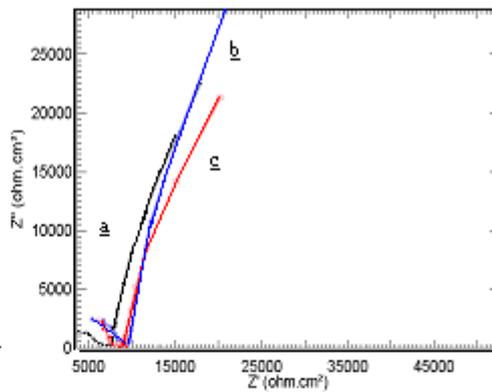


Fig.3b:
OPC+1%Cl⁻

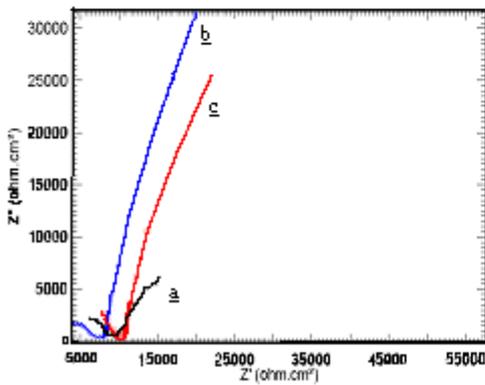


Fig.3c: OPC+2%Cl⁻

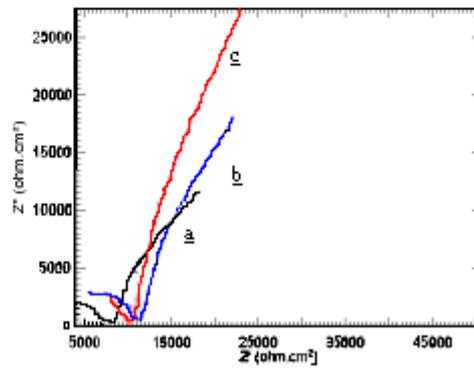


Fig.3d: OPC+3%Cl⁻

Fig.3. Nyquist plots of TMT steel embedded in OPC concrete admixed with various levels of chloride

a - control, b - Migrating (MI), c - Electro injection (EI),

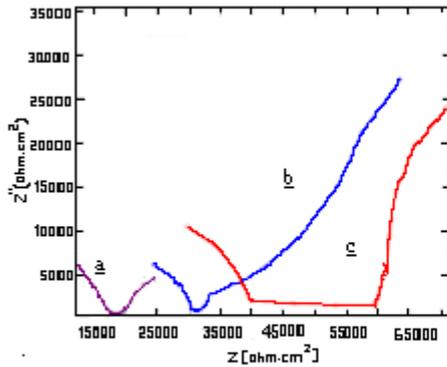


Fig.4a: PSC

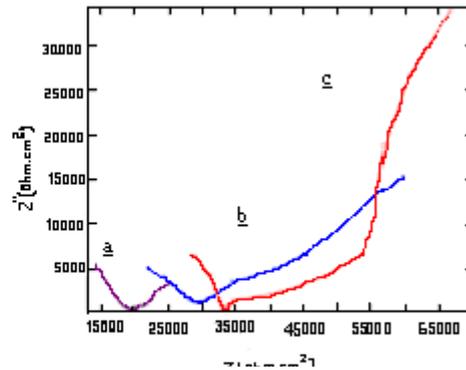


Fig.4b: PSC+1%Cl⁻

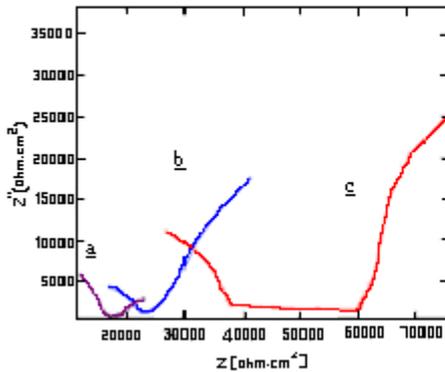


Fig.4c: PSC+2%Cl⁻

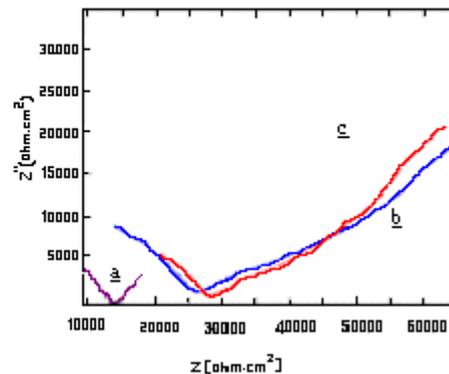


Fig.4d: PSC+3%Cl⁻

Fig.4. Nyquist plots of TMT steel embedded in PSC concrete admixed with various levels of chloride EI- a - control, b - Migrating (MI), c - Electro injection (EI),

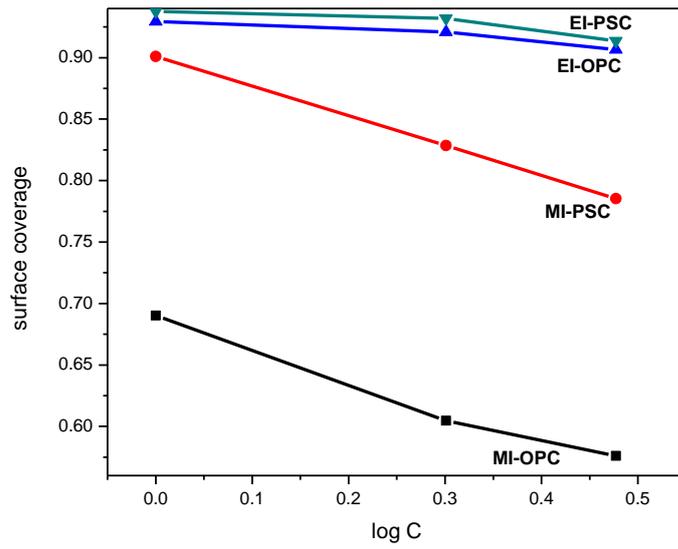


Fig.5. Temkin adsorption isotherm

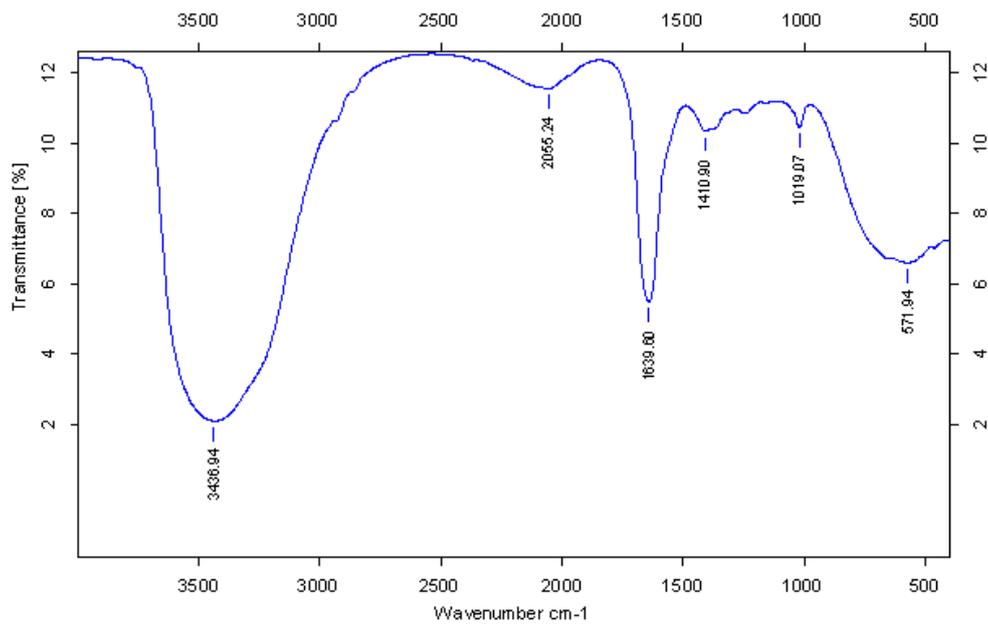


Fig.6. FT-IR Spectra of OPC after EI treatment

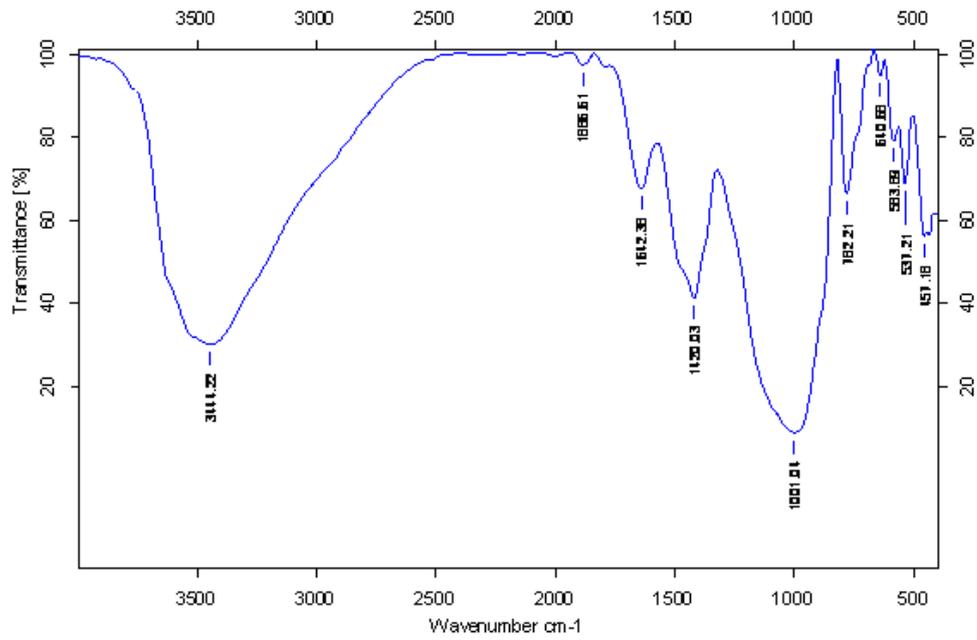


Fig.7.FT-IR Spectra of PSC after EI treatment