

Evaluation of concrete performance incorporated with amine group corrosion inhibitor

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ABSTRACT

The current investigation concentrates on evaluating the performance of inhibitors added to concrete to resist corrosion. Specimens were cast with different mix proportions involving various combinations of inhibitors of M30 grade prepared as per Indian standards. For investigating the performance of inhibitors added in the concrete of M30 grade various tests such as pH measurement, Weight loss measurement, OCP otherwise known as rest potential measurement, impressed voltage, Rapid Chloride Penetration test and determination of chloride diffusion coefficient were conducted. To evaluate the strength parameters tests were conducted on the casted specimens of concrete. The tests include compression strength test, flexural and strength test. Results indicated that amine compound-based inhibitor has a more pore-clogging impact which blocks chloride ingress. The polarization and impedance behavior of steel in concrete after the electrochemical injection process exhibited a considerable reduction in the occurrence of the rate of corrosion in steel reinforcement despite the severe chloride ions. IR spectra observations recorded the existence of inhibitor molecules on the embedded steel surface.

Keywords: Corrosion inhibitor; Corrosion efficiency; Concrete strength; Chloride diffusion coefficient; IR spectroscopy.

1. INTRODUCTION

Metals are subject to corrosion, which is a destructive attack caused by an environment-driven chemical or electrochemical process. Corrosion can manifest itself in a variety of ways, such as reddish-brown rust on steel, copper and silver by tarnishing, and the formation of a white substance on zinc. The definition of corrosion excludes plastic swelling, wood rot, granite erosion and Portland cement leaching. In the context of iron and iron base alloys, “rusting” explicitly refers to corrosion. Concrete is inherently durable under normal exposure conditions. In most cases of structural failure, corrosion of reinforcements in concrete structures results in the reduction of the life span of the structure [1]. So, this problem poses a major threat to offshore and coastal structures. In the marine environment, corrosive salts enter into the pores of the concrete and thus result in accelerated rusting of rebars leading to structural failures at an earlier age than expected. The corrosion of reinforcing steel used in concrete structures due to chloride exposure is a prevalent phenomenon, characterized by its intricate nature encompassing structural, physical, chemical, and environmental factors [2]. More effort has been taken in the initial stages of design to reduce the occurrence of corrosion by providing proper concrete cover which ensures the reduction in permeability of concrete. Concrete structures exposed to chlorides show an increased rate of deterioration as compared to those structures with no chloride contamination of the concrete. The contamination may be due to saline contamination of aggregates or water used in the batching of concrete or from direct exposure to marine environments [3]. The occurrence of corrosion in steel is greatly controlled by numerous variables such as moisture content, carbonation attack, chloride intrusion, oxygen availability, pH level, concrete quality, presence of cracks, electricity resistivity and environmental conditions. Among the listed factors, the effect due to chloride ingress in concrete affects the durability of the concrete causing structural failure [4]. To overcome the problems related to corrosion in steel reinforcement, various preventive measures such as coatings to concrete and reinforcement, steel reinforcement protection measures through cathodic protection techniques, and adding inhibitors have been already investigated by several researchers [5–7]. For the present research,

adding corrosion inhibitors in concrete is taken for the study. Corrosion inhibitors are substances introduced into concrete in small quantities, designed to be compatible with the material and not provoke undesirable reactions or adverse changes in its physical characteristics. Furthermore, they should offer cost-effectiveness compared to alternative corrosion control methods [8]. Corrosion inhibitors exert an impact on the rate of corrosion processes by influencing the kinetics of electrochemical reactions that drive these processes. They accomplish this by effectively slowing down the anodic reaction, the cathodic reaction, or both simultaneously [9]. While inhibitors find extensive application in corrosion technology, their utilization for controlling steel corrosion in concrete has been restricted due to the diverse array of environments structures encounter and their potential effects on the various properties of concrete induced by the presence of said inhibitors. Corrosion inhibitors emerge as an appealing choice for safeguarding steel against corrosion in concrete when exposed to chloride ions. Within the concrete environment, the interplay between chloride and hydroxide ions can lead to significant corrosion of embedded steel, particularly when oxygen is present to facilitate the cathodic reaction [10]. GOYAL *et al.* [11] studied the efficiency of organo-functional-based corrosion inhibitors. Chemical compounds such as nitrites, benzoates and phosphates were also utilized as corrosion-inhibiting substances in concrete. According to LING *et al.* [12] the substantial decrease in concrete strength caused by sodium benzoate raises concerns about its utilization in significant quantities, prompting further questioning regarding its practical application. The use of sodium benzoate has been found to have a detrimental effect on the concrete's yield strength. Used mainly for protecting concrete structures that are either reinforced or prestressed due to its corrosion inhibition property, calcium nitrate has gained popularity over the past fifteen years. Nevertheless, a substantial discussion continues concerning the effectiveness and practicality of corrosion-inhibiting admixtures. The aforementioned studies have collectively demonstrated that no individual inhibitor is capable of providing adequate protection to steel in concrete. Therefore, a formulation comprising two or more inhibitors (of the multi-functional type) is required to ensure sufficient protection of the steel in concrete. The main aim of this study is to assess the competence of an amine-based corrosion inhibitor when added to concrete and investigate its impact on both the fresh and hardened concrete properties. Workability aspects of the concrete were evaluated through the slump cone test and flow table test. The hardened concrete properties were assessed by performing tests for splitting tensile strength, compressive strength, and flexural strength. Corrosion resistance in embedded reinforcement was measured by pH measurement, Weight loss measurement, OC potential measurement, Impaired voltage, Rapid Chloride Penetration test and determination of chloride diffusion coefficient.

2. MATERIALS AND METHODS

2.1. Materials used

The physical properties of the commercially available amino acid corrosion inhibitors and inorganic nitrite are shown in Table 1. At room temperature ($25^{\circ}\text{C} \pm 1^{\circ}\text{C}$), the pH of the saturated $\text{Ca}(\text{OH})_2$ solution was measured and found to be 12.8. The pH was determined after adding different amounts of Na_2SO_4 to a saturated $\text{Ca}(\text{OH})_2$ solution that contained 0.98 g/L of NaCl. pH measurements were done after the solutions were created since mixed solutions are sensitive to pH changes. The $\text{Ca}(\text{OH})_2/\text{NaCl}/\text{Na}_2\text{SO}_4$ solutions were then combined with corrosion inhibitors in different quantities. The 16 mm-diameter steel specimens were then chopped and placed in thermosetting resin that was resistant to acid and alkali. The samples that were mounted were polished using sandpaper that had a size range of 180 to 1,200 μm . The goal of the study was to simulate the conditions of concrete by examining the effects of inhibitors on corrosion resistance and pH of solutions with different amounts of sulfate and chloride ions. This was accomplished by introducing different corrosion inhibitors to change the quantity of sulfate ions while maintaining a consistent concentration of chloride ions in the $\text{Ca}(\text{OH})_2$ solution. After that, electrochemical experiments were performed to evaluate the effectiveness of four distinct corrosion inhibitors.

Table 1: Physical characteristics of corrosion inhibitors.

TYPE OF INHIBITOR	CHEMICAL FORMULA	pH	VISCOSITY	SPECIFIC GRAVITY	SOLID LEVEL (%)
Diethanolamine	$\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$	12.72	8.14	1.048	74.00
Lithium nitrite	LiNO_2	12.07	10.07	1.082	91.24
Methyl diethanolamine	$\text{C}_5\text{H}_{13}\text{NO}_2$	11.32	11.15	1.027	91.24
4-Aminobutyric acid	$\text{H}_2\text{N}(\text{CH}_2)_3\text{COOH}$	8.08	9.11	1.121	79.65

2.2. Cement

Ordinary Portland cement (OPC) conforming to IS: 8119-1989 [13] was utilized as it is commercially available cement in the market. However, the production of OPC causes environmental pollution as an approximately equal volume of carbon dioxide is liberated during the production of OPC. To avoid these greenhouse gas emissions, now-a-days blended cements have come into use and hence Portland pozzolana cement (PPC) conforming to IS: 1489 (Part-1) 1991 [14]; fly-based and Portland slag cement (PSC) which confirms to IS: 455-1989 [15] were chosen for the study. Since the presence of pozzolana in PPC and slag in PSC it is expected to make a difference in the ability of steel to resist corrosion when used in concrete. For improved corrosion protection of steel, corrosion inhibitors are added to reduce the corrosion attack in steel reinforcement. The inhibitor efficiency depends on the category of organic, inorganic, or polymeric. In this investigation, amine group inhibitors named Diethanolamine, Lithium nitrate, Methyl diethanolamine and 4-Aminobutyric acid are used. These inhibitors have a common anion NH_2^- and a common cation NH_4^+ . In the present study, both conventional weight loss and various electrochemical D.C and A.C techniques were employed to examine the performance of inhibitor formulation on concrete. OCP of rebar in various systems was monitored periodically as per ASTM C-876-2000 [16]. The weight loss method yields a true corrosion rate for reinforcement incorporated along with concrete in the presence of inhibitors and chlorides.

2.3. Characterization studies

2.3.1. pH measurement

Using a 90 μm sieve, the concrete is sieved and a sample of 50 g of this sieved cement was used to make the extracts. For preparing the extracts, the 50 g cement and 100 ml of distilled water were mixed and vigorously agitated with the help of a Microid flask mechanical shaker for an hour. These were then procured by the process of filtration. Using a Model 76 P potable Istek Inc. pH meter, the pH of the extract was measured as shown in Figure 1. pH 9.2 buffer solution was used for the pH meter calibration. At least 3 readings were taken for each system and the average pH value was noted. The pH of PPC, OPC, and PSC was 12.35, 12.76, and 12.52 respectively.

2.3.2. Weight loss measurements

Rods of diameter of 12 mm and length of 70 mm were subjected to cleaning in the pickling solution according to ASTM-G-90 [17]. Once cleaned, the TMT (Thermo-Mechanical Treatment) rods were washed with the help of water and dried. The initial weight of the bars was measured. Then these bars were embedded into the concrete mix specimen that contained 0–3% of chloride admixture which was added to induce corrosion and then kept in water for curing for twenty-eight days. After the specimens were cured, they were taken away for migrating and electro-injection. Once all the other tests had been completed, the weight loss test was carried out. For this, the rebar in the concrete was extracted by breaking the concrete open and cleaned by being kept in the pickling solution and then washed under water and dried. After this, the final weight is found out. The casted specimens

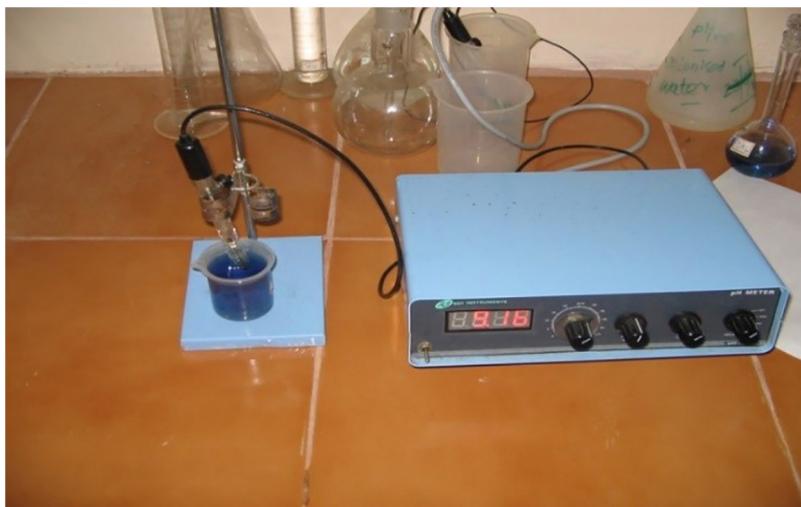


Figure 1: Experimental Set up for pH measurement.

were weighed again and the weight loss was calculated. From those values, the rate of corrosion was obtained from the given Equation 1.

$$\text{Corrosion rate} = \frac{8.76 \times W}{D \times A \times T} \quad (1)$$

Where, W = lost weight (mg) D = material density (g/cm³) T = time (hours) and A = specimen area (cm²).

2.4. Tests of properties of concrete

2.4.1. Compressive strength

For carrying out the compressive strength test, 100 × 100 × 100 mm sized specimens of 1:1.80:3.696 and w/c ratio as 0.50 concrete was used. The specimens were cast with both with and without admixture of inhibitors. During the casting of specimens, they were mechanically vibrated for twenty-four hours and then removed from the mould. They were then kept in water for curing for twenty-eight days. After the curing was carried out, with the aid of AIMIL CTM of 2000 kN capacity, the specimens were tested at a loading rate of 140 kN/min. At least three specimens underwent the tests, and the average result was note.

2.4.2. Open circuit potential measurement

A 50 mm diameter and 100 mm long specimens of concrete were cast with 12 mm diameter and 20 mm long rebars that were cleansed using pickling acid and degreased embedded in them, providing a 15 mm bottom cover. Specimens for concrete with and without the inhibitor were cast. After being cured for twenty-eight days, the specimens were subjected to drying for 24 hours. Then the specimens underwent cycles of wetting and drying in a 3% NaCl solution to hasten the corrosion of reinforcement. One cycle involves immersing the object in the solution for three days and then drying it in the environment for an additional three days. The OCP readings were obtained and assessed using a voltmeter equipped with a high input impedance of 10 megaohms. The common terminal was linked to the saturated calomel electrode (SCE) which served as the reference electrode. The positive terminal was attached to the rebars, which were taken as the working electrode. The measurements were recorded from three different points on the rebar, proximal to it, and the average was calculated. The results were then used to plot the potential vs. time graph. Figure 2. shows the experimental setup of open circuit potential measurement.

2.4.3. Impressed voltage test

To compare the different properties of concrete, the accelerated corrosion testing method is carried out by conducting the impressed voltage test. For this method, the specimen was submerged in a three per cent solution of NaCl and then steel in the concrete was made out to be the anode and as cathode, an external stainless-steel electrode was used. A constant positive 12V DC potential is applied to the system. A steep rise in the current suggests that the corrosion has begun and the concrete cracking is visible thereafter. Figure 3 shows the schematic



Figure 2: Experimental set-up for open circuit potential measurement.

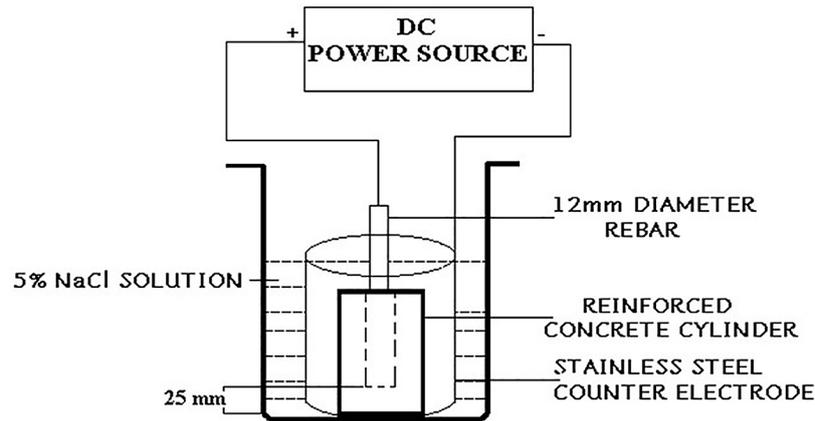


Figure 3: Schematic representation of impressed voltage test.



Figure 4: Schematic representation of Rapid Chloride Permeability test.

representation of the arrangement of the test. The duration of the first fracture can be used to gauge the reinforcement's relative resistance to corrosion and the permeability of their chloride.

2.4.4. Rapid Chloride Ion Penetration Test (RCPT)

As per ASTM C 1202 [18], the resistance against penetration of ions of chloride in the context of total charge passed in Coulombs through the specimens after twenty-eight to ninety days of moisture curing is measured. The specimens had a size of 98 mm diameter and 50 mm thickness and were cast and cured for 28 days. After curing, the specimens then underwent an RCPT test by impressing 60V as shown in the photograph given below in Figure 4. A PVC container of size 100 mm in diameter was used to seal the 2 halves of the specimen. Each side of the container is either filled with 3% NaCl(aq) or 0.3N NaOH(aq). The side of the power supply that contains the NaCl is linked to its negative terminal, while the side that contains the NaOH is connected to its positive side. The current was measured every thirty minutes up to 6 hours. Temperature as well as chloride contamination was also evaluated and monitored every 30 minutes. At the conclusion of the test period, the permeability to chloride ions is computed in terms of Coulombs based on the acquired data. The cumulative charge passed is a measure of the conductance of the concrete during the duration of the test.

2.4.5. Application of inhibitor formulation into concrete

Specimens of OPC, PPC, and PSC concrete in the shape of cylinders with the size of 60 mm diameter and 100 mm height were cast with different percentages of NaCl ranging from 1% – to 3% based on the cement weight. At the center of each specimen, a rebar of 12 mm diameter and 70 mm length was embedded. The mix

Table 2: Migration and electrochemical formulation.

S. NO.	CHEMICAL NAME	CONCENTRATION
1.	Diethanolamine	0.25M
2.	Lithium nitrite	0.05M
3.	Methyl diethanolamine	0.25M
4.	4-Aminobutyric acid	0.25M

Table 3: Admixed process formulation.

S. NO.	CHEMICAL NAME	CONCENTRATION
1.	Diethanolamine	0.025M
2.	Lithium nitrite	0.025M
3.	Methyl diethanolamine	0.025M
4.	4-Aminobutyric acid	0.025M

**Figure 5:** Inhibitor applied on the surface of the concrete specimen – migration process.

design of the specimens was 1:1.8:3.69 with W/C as 0.50. The specimens underwent mechanical vibration at the time of casting and were then demolded after 24 hours. To avoid any contamination, they were then cured in distilled water for twenty-eight days. The inhibitor concentration for migration and electrochemical formulation is given in Table 2.

2.4.6. Admixed properties

In this process, during the mixing stage, the addition of the inhibitor is carried out to avoid any contamination, distilled water was used for curing for twenty-eight days after it was demolded. After curing, the specimens were kept at room temperature. Table 3, depicts the concentration of inhibitors for the admixed process formulation.

2.4.7. Migrating and electro injection process

On the external surface of the specimen, the inhibitors are applied either by spraying or by brushing and repeated 3 times at an interval of 24 hours as shown in Figure 5. The required amount of the inhibiting action was achieved in fifteen days. TMT rebar embedded in concrete specimens and perforated cylindrical stainless steel

plate act as cathode and anode respectively. A 2000 ml of electrolyte was taken in the electrolytic cell and a current density of 1 A/m² was Galvano statically maintained for an exposure period of 7 days.

2.4.8. Microstructural analysis of concrete aggregates

Under various experimental conditions, the surface properties of three distinct concrete mixes (OPC, PPC, and PSC) were investigated using scanning electron microscopy (SEM) in conjunction with energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR). In order to improve the mechanical strength of concrete mixes, the efficiency of the inhibitors and their interactions with concrete particles were investigated through the analyses. The best mixtures, which were identified based on each concrete mix's mechanical strength findings in this study, underwent microstructural investigation.

3. RESULTS AND DISCUSSION

3.1. pH measurements

Table 4 shows the details about the pH values of OPC, PPC, and PSC specimens for plain and those which contain chlorides and inhibitor formulation as well. The pH values of plain extracts were found to be between 12.29 and 12.70 for OPC, PPC and PSC. The pH values for extracts containing chlorides and inhibitor formulation were found to be between 11.90 and 12.85 for OPC, PPC and PSC systems respectively. These data indicate that the addition of inhibitor formulation did not affect the alkalinity that much. Hence this inhibitor formulation is found to be suitable for use in concrete [19].

3.2. Compressive strength

Table 5, shows the compressive strength results of concrete specimens added with and without admixture. The compressive strength for a specimen containing admixture does not affect the controlled specimen and was found to be increasing. Referring to the Table 5, the compressive strength of concrete mixes (OPC, PPC and PSC) were increased by adding inhibitors into the concrete mixes. Also, a small amount of increase represents the minor changes in compressive strength of the concrete mixes at 28 days of curing time.

Table 4: Comparison of pH values for various systems.

SYSTEM	CHLORIDE (%)	SPECIMEN NUMBER	pH			
			PLAIN	ADMIXTURE	MIGRATION	E-INJECTION
OPC	0	1	12.52	12.24	12.65	11.90
	1	2	12.59	12.23	12.46	12.01
	2	3	12.49	12.25	12.73	12.04
	3	4	12.34	12.23	12.55	12.16
PPC	0	5	12.41	12.15	12.30	12.33
	1	6	12.61	12.20	12.67	12.22
	2	7	12.54	12.30	12.34	12.31
	3	8	12.70	12.23	12.44	12.42

Table 5: Compressive strength of OPC, PPC and PSC concretes with mix ratio of (1:1.80:3.69).

CONCRETE	WITHOUT INHIBITOR AFTER 28 DAYS (N/mm ²)	WITH INHIBITOR AFTER 28 DAYS (N/mm ²)
OPC	34.44	36.45
PPC	32.21	33.89
PSC	33.82	34.25

3.3. Potential time and Inhibitor system

The inhibitor is mixed with concrete and various levels of chloride from 0% to 3%. The behavior of TMT steel in OPC, PPC and PSC concrete admixed with 0%, 1%, 2% and 3% NaCl along with inhibitor formulation is shown below by datum and graph of Open circuit potential and Impressed voltage tests. Table 6. and Figure 6. show the Open circuit potential measurements taken for different systems under wet and dry conditions. From the figure it is perceived that all the systems have shown more negative potentials than -275 mV vs. SCE irrespective of the exposure conditions whether it is wet or dry conditions.

3.4. Impressed voltage test

Figures 7a, b and c show the current vs. time behavior of PSC, PPC, and OPC concretes with and without admixed systems. From the figure it is found that the admixed systems can perform better than the control systems indicating lesser flow of anodic current. Among the three cements studied PSC is found to have better performance when compared with the other two systems. This is because higher alumina present in PSC combines with chlorides forming Friedel’s salt called Calcium chloro aluminates [20].

3.5. Potential time behavior of migrating system

Figures 8a, b and c represent the potential-time behavior of TMT steel in OPC, PPC and PSC concretes with and without chloride ranging from 1% to 3%. The potential was checked for 14 days. From the figures it is found that as the concentration of chloride increases, the potentials were found to be shifted to a more negative direction. From the results it is observed that OPC and PSC concretes are found to perform better than the PPC concretes. This is because, PPC contains 25% fly ash which depletes the OH- concentration and reduces the pH, which

Table 6: Open circuit potential (OCP) measurements in dry and wet conditions.

SPECIMEN NO.	EXPOSURE PERIOD/DAYS DRY CONDITION						EXPOSURE PERIOD/DAYS WET CONDITION					
	1	4	7	10	13	16	1	4	7	10	13	16
	1	-0.273	-0.366	-0.216	-0.217	-0.268	-0.262	-0.311	-0.405	-0.395	-0.385	-0.334
2	-0.268	-0.35	-0.286	-0.275	-0.295	-0.319	-0.567	-0.445	-0.512	-0.451	-0.524	-0.66
3	-0.344	-0.369	-0.296	-0.299	-0.301	-0.295	-0.601	-0.49	-0.521	-0.476	-0.56	-0.654
4	-0.364	-0.378	-0.305	-0.321	-0.324	-0.28	-0.589	-0.534	-0.533	-0.464	-0.534	-0.64
5	-0.335	-0.364	-0.31	-0.312	-0.335	-0.271	-0.6	-0.544	-0.551	-0.504	-0.55	-0.68
6	-0.35	-0.385	-0.334	-0.3	-0.321	-0.265	-0.57	-0.567	-0.594	-0.486	-0.5	-0.675
7	-0.375	-0.37	-0.325	-0.311	-0.331	-0.3	-0.55	-0.58	-0.603	-0.473	-0.576	-0.693

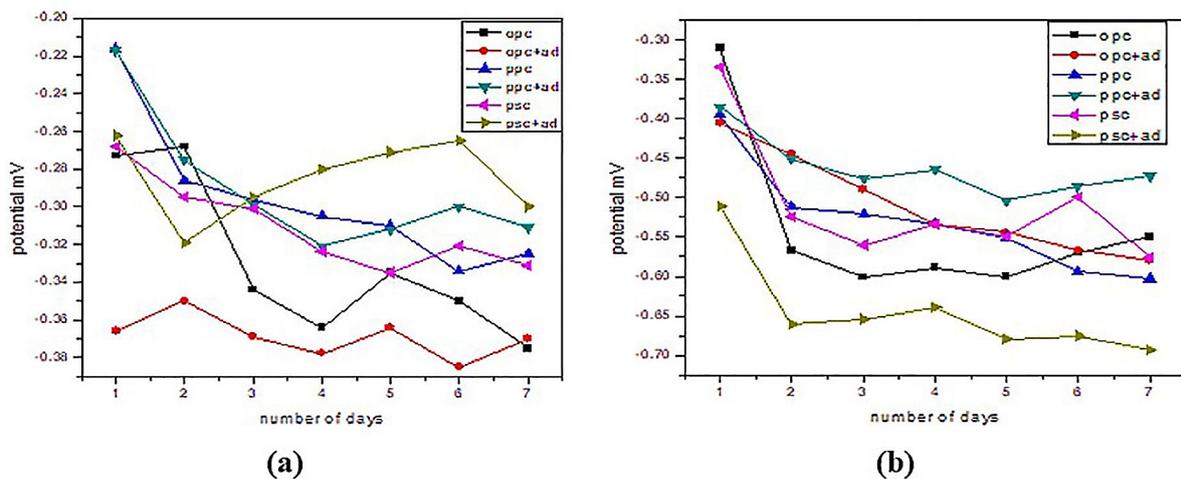


Figure 6: Open circuit potential measurements taken for different systems under (a) dry and (b) wet conditions respectively.

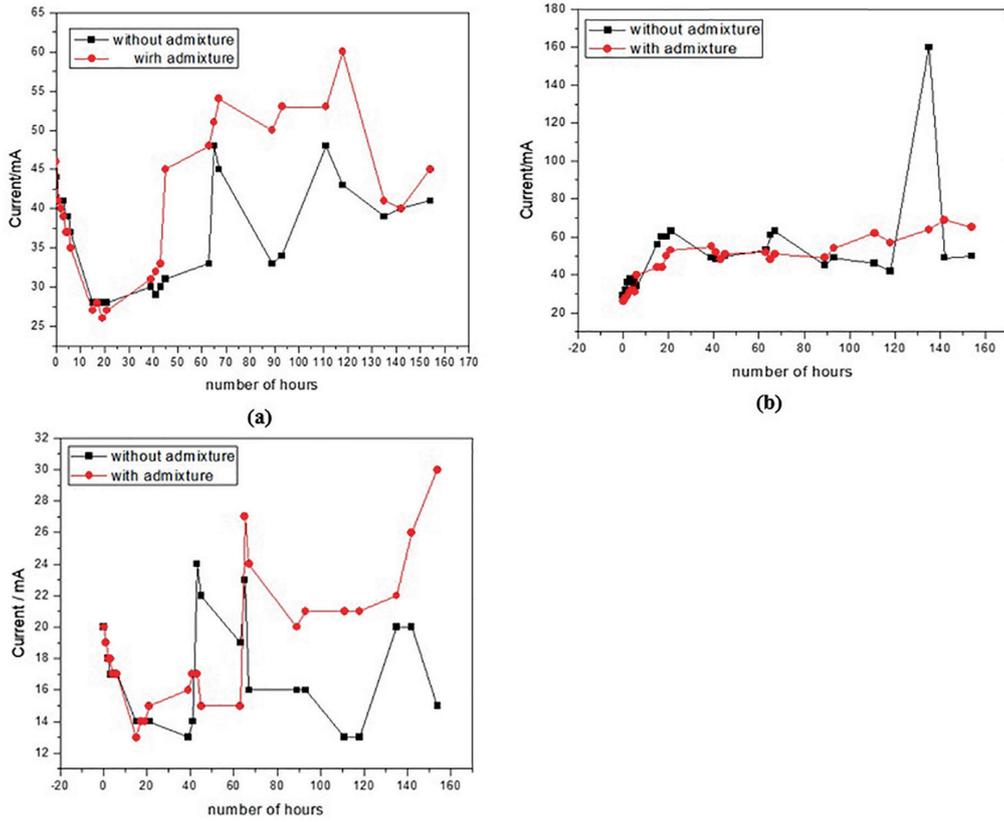


Figure 7: Current vs. time behavior of TMT steel embedded with (a) OPC, (b) PPC and (c) PSC in impressed voltage test.

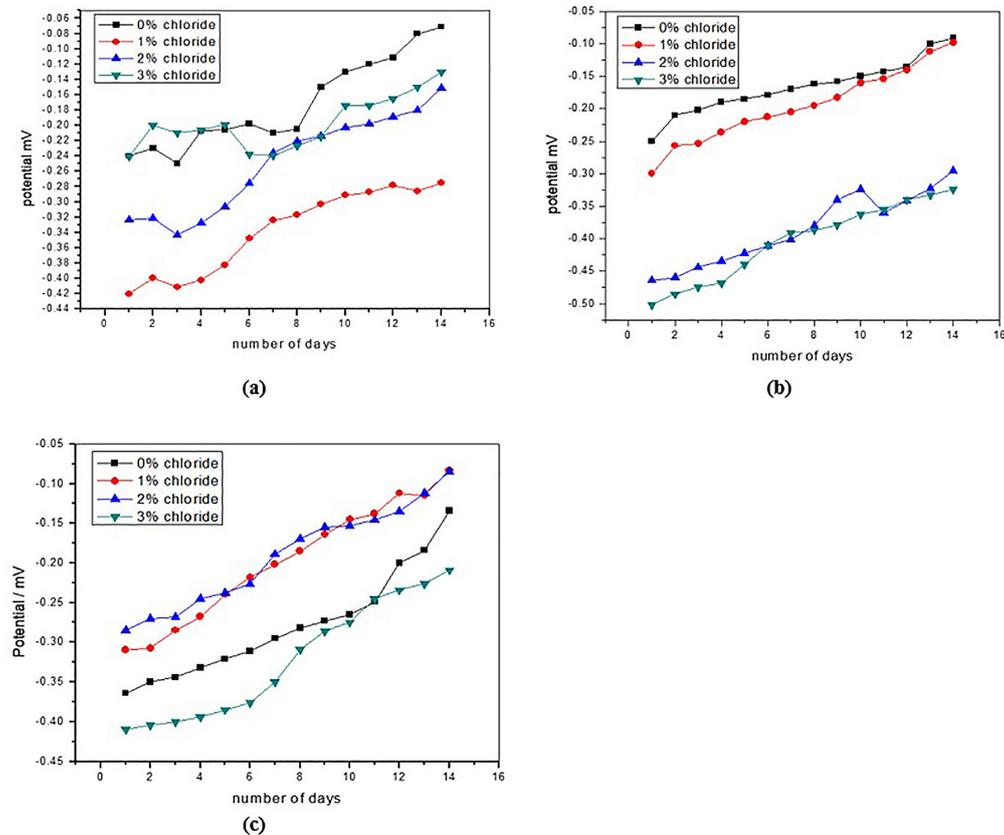


Figure 8: Potential-time behavior of (a) OPC, (b) PPC and (c) PSC concrete in migrating system.

leads to higher porosity [21]. PSC also contains 70% slag and 9% alumina enhancing the complex formation of Friedel's salt and pore size refinement which enhanced the corrosion resistance performance [22].

3.6. Potential time behavior of electro injection inhibiting system

The potential-time behavior of TMT steel embedded in OPC, PPC and PSC concretes admixed with 0%, 1%, 2% and 3% NaCl for electro-injected specimens are shown in Figures 9a, b, c and d respectively. It was recorded that novel inhibitor formulation shifted the potential of rebar towards a more positive direction. After 7 days, by carrying out the Open Circuit Potential of TMT steel was observed as -160 mV, and -120 mV for systems with electro-injection. The specific discovery reveals that an inhibitor formulation capable of electrochemical injection into concrete may reach steel, shifting potential in the direction of anodization and shielding rebar from very corrosive environments [23]. The passivation of the surface of steel by the inhibitors resulted in corrosion inhibition. According to potential-time experiments, the new, unique inhibitor formulation was far more appropriate for the electro-injection process into the concrete when there were more chloride ions present. Completed within seven days of conception, which can be taken as a reasonable amount of time, the process is deemed to be successful. It was then completed triumphantly in the short duration of a week which can be implemented for concrete structure repair and rehabilitation [24]. Among the three concrete specimens used, the one where PPC was used performed better than the others in all three chloride levels.

3.7. Rapid chloride penetrability test (RCPT) and chloride diffusion coefficient

Table 7, shows the Coulomb values and chloride diffusion coefficient obtained under steady-state conditions from the RCPT test. From the table, it is observed that the admixed systems are found to have lesser coulomb values indicating the lower permeability of the concrete. Among the systems studied PSC concrete is found to have lesser coulomb values indicating better performance. The addition of an inhibitor reduces the effect of chloride ions passing through the specimen, reducing the amount of pores in the specimen [25].

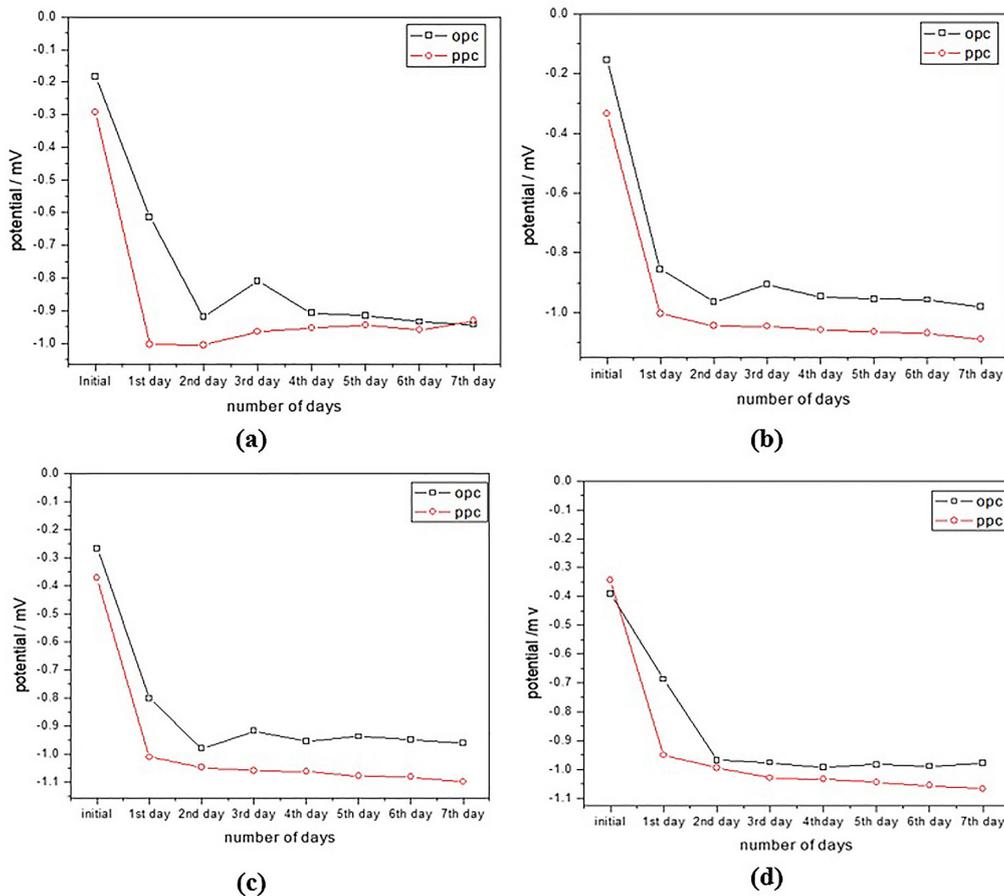


Figure 9: Potential-time behavior of electro-injection of the inhibiting system into concrete for (a) 0% Cl⁻, (b) 1% Cl⁻, (c) 2% Cl⁻ and (d) 3% Cl⁻ respectively.

Table 7: Coulomb, chloride diffusivity coefficient values for OPC, PPC and PSC from RCPT test.

SYSTEMS	CHLORIDE PPM	FLUXIONS(J) ($\times 10^{-9}$)	CHLORIDE DIFFUSIVITY(D) ($\times 10^{-12}$)	COULOMB	REMARKS
OPC	2481.71	1.473	6.187	2062.82	Medium
OPC + ADMIXTURE	1985.37	1.179	4.951	1971.98	Moderate
PPC	3084.41	1.832	7.692	2012.45	Medium
PPC + ADMIXTURE	2197.98	1.305	5.488	1605.64	Moderate
PSC	2446.25	1.453	6.102	869.43	Low
PSC + ADMIXTURE	1985.36	1.18	4.955	723.22	Low

Table 8: Comparison of corrosion rate of admixed, migrating, and electro-injection of inhibiting systems by Weight loss method.

SYSTEM	CHLORIDE (%)	CORROSION RATE (mm/y)		
		PLAIN	MIGRATING ($\times 10^{-4}$)	E-INJECTION ($\times 10^{-5}$)
	0	0.0348	0.879	6.06
OPC	1	0.135	0.053	3.03
	2	0.1421	0.338	1.099
	3	0.2011	1.093	0.55
PPC	0	0.0345	0.655	0.526
	1	0.0455	0.756	0.53
	2	0.0589	0.252	0.53
	3	0.201	0.125	0.526

3.8. Weight loss measurements

The corrosion rate for TMT steel in OPC and PPC concretes containing inhibiting formulations admixed with various amounts of chlorides (0%, 1%, 2%, and 3%) is shown in Table 8. It can be concluded that the E-injection process showed the lowest rate of corrosion when compared to other methods. In the case of OPC, 3% chloride level without inhibitor (Plain) showed a corrosion rate of 0.0348 mm/y. Systems showing less than 0.0348 mm/y may be considered a better inhibiting system in OPC concrete. The steel's corrosion rate in OPC concrete with a 3% chloride level is 0.2011 mm/y, 0.0001 mm/y and 0.00005 mm/y respectively for plain, migrating and E-injection processes. When it comes to PPC concrete, steel's corrosion rate in the control specimen was found to be 0.0345 mm/y for 0% chloride, 0.0455 mm/y for 1% chloride, 0.0589 mm/y for 2% chloride and 0.201 mm/y for 3% chloride.

All the inhibited systems displayed a lowered rate of corrosion than control systems. At a 3% chloride level, the rate of corrosion of numerous systems follows the order:

$$\text{Plain} > \text{Migrating} > \text{E-injection}$$

$$0.2011 \text{ mm/y} > 0.0001 \text{ mm/y} > 0.00005 \text{ mm/y}$$

For the inhibiting processes, the reduction in the rate of corrosion follows the order:

$$\text{Electro-Injection} > \text{migrating}$$

$$49\% > 24\%$$

Because an insoluble complex but stable film was formed through the chemisorption procedure over the metal's surface, inhibition occurs. The formation of the film leads to inactive anions. With both the inhibition

and inactive anions, passivity on the steel surface develops even if it is under higher concentrations of aggressive anions [26]. The reduction in the steel's corrosion rate of various samples, and weight loss data can be given below:

$$\text{PPC} < \text{OPC}$$

Despite being in the presence of 3% chloride, the formulation was found highly effective in aiding to reduce the steel's self-corrosion. Natural seawater usually contains 3% chloride. Here, it is interesting to note that this mixed inhibitor formulation performed well in 3% chloride. Thus, this formulation is reasonably suitable for our requirement to use it in marine environments as well.

3.9. Microstructural analysis of concrete mix with inhibitors

The microstructure of cement-based materials has a major impact on the properties of cured concrete. Using scanning electron microscopy (SEM), the morphology of the matrix and the microstructure of the concrete were investigated. After 28 days of curing, three SEM micrographs of the OPC, PPC, and PSC concrete mixes were taken. The OPC mix micrograph (Figure 10a) shows a denser and more homogenous microstructure than the PPC and SPC mix micrographs (Figures 10b and 10c, respectively). The smaller OPC grains cause a reduction in pore size during the hydration process, which aids in the refining of the pore structure [27]. The combination combining PPC and SPC demonstrated higher compressive strength, according to the experimental results regarding mechanical characteristics. This mixture's increased strength is a result of the C-S-H gel's presence. The CH area increased for the OPC, PPC, and SPC mixes relative to the control mix by 0.340%, 8.214%, and 3.210%, respectively. This finding is corroborated by the EDS data (Figures 11a, b and c), which show the amount of calcium hydrate in OPC, PPC, and PSC with inhibitors. With a higher superplasticizer ratio came a lower C-S-H content, which in turn led to a lower silicate hydrate (Si) content and a higher CH content. More porosity was made possible by the reduction in C-S-H. The decrease of C-S-H bonds while utilizing inhibitors has also been the subject of previous research investigations [28–30]. The compressive strength and porosity test results obtained by the methanol exchange approach ultimately agree with the findings obtained from the EDS and SEM studies. In order to investigate the corrosive products in the concrete caused by sulfate attack, an X-ray diffraction study was carried out for the OPC, PPC, and PSC mixes with inhibitors. The XRD diffractograms are shown in Figure 12. The intensity peaks of C-S-H and portlandite in the 200-cycle OPC sample (Figure 12a) were

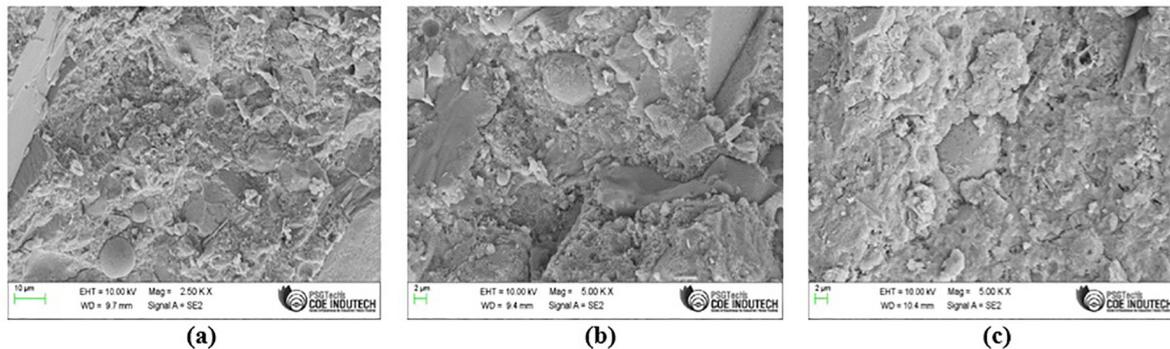


Figure 10: SEM images of (a) OPC and (b) PPC and (c) PSC concrete mix with inhibitors.

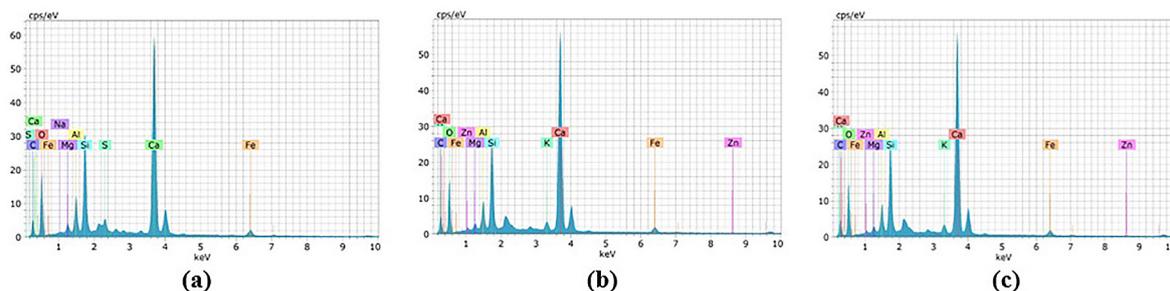


Figure 11: EDS images of (a) OPC and (b) PPC and (c) PSC concrete mix with inhibitors.

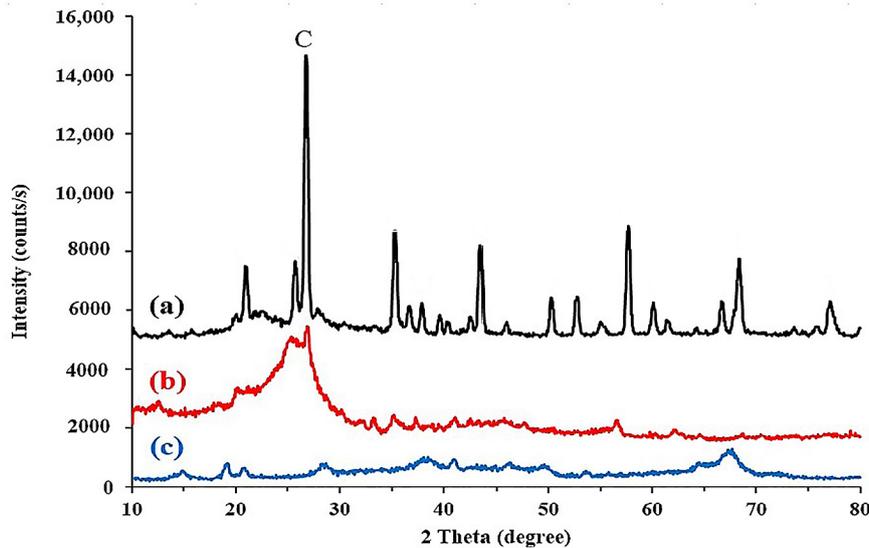


Figure 12: XRD images of (a) OPC and (b) PPC and (c) PSC concrete mix with inhibitors.

comparatively smaller than those in the PPC sample (Figure 12b). In a similar vein, Figure 12c shows the XRD peaks of the PSC concrete mix. There were additional traces of thenardite and gypsum found in Figure 12a. The material peaks became more intense following exposure. This suggests that although C-S-H and portlandite are consumed, gypsum, thenardite, and the material are produced with cyclic sulfate exposure [31]. According to the XRD results, the OPC mix's crystalline structures are more noticeable than those of the PPC and PSC mixes. The OPC mix's peaks were clearly visible at matches with 80, 110, 60, 40, 30, and 20 hkl planes at 140, 210, 260, 291, 370, and 450. This demonstrates that the OPC mix pitches at a far higher intensity than the PPC and PSC mixes.

4. CONCLUSIONS

Recognized to act as a corrosion inhibitor in aqueous solution for steel, two main organic bases were added to concrete through admixing, migrating, and electro-injection. The added organic bases, i.e., amine and ester-based inhibitors, have mainly two functions. The amine compound performs the inhibiting function, whereas the carboxylate ester compound cancels the ingress of chloride due to its pore-blocking ability. Due to their low cost and easier-to-handle property, corrosion-inhibiting admixtures are preferred over the available methods. The inhibitor formulation is applied to fresh concrete for new structures. The surface-applied migrating corrosion inhibitor penetrates the hardened concrete and is usually proposed for repair systems, while admixed inhibitors were commercially available in the 70s, migrating corrosion inhibitors for concrete structures were proposed in the last 5–10 years. In the above two methods, the reactions were carried out without applying current density. But in electro injection method, the inhibitor is applied from the external electrolyte under the influence of an electrical field applied between the embedded steel cathode and external anode. The cathodic current density was galvanostatic Ally controlled at the values in the range of 1 A/m² for a period of 1 to 7 days and released free chloride was analyzed. The electrochemical measurements show the electro-injection method has high inhibiting efficiency among the other methods for protecting the steel from corrosion. Electro-injection of inhibitors into concrete is considered one of the easy repair and rehabilitation strategies for civil infrastructures. In the present study, a new multi-component inhibitor formulation was designed. The composition was introduced into PSC, OPC, and PPC using the electro-injection technique. Even with strong chloride ions present, the rate of corrosion was significantly reduced as a result of the steel's polarization behavior in concrete following the electro-injection procedure.

The given general insights can be drawn from this investigation:

- The new multi-component inhibitor formulation consists of pore-blocking, inhibiting ions, passivating ions, and transporting ions found effective in concrete environments for the protection of steel-resisting chlorides.
- This inhibitor formulation can be injected into concrete at the cathode current density of 1 A/m².
- Within the exposure duration of seven days, the rebar potential changed towards a more positive direction amidst chloride presence as suggested by the potential-time investigations conducted.

- The polarization behavior of steel in concrete containing electrochemically injected inhibitors showed a considerable reduction in corrosion rate despite being in the premises of an aggressive chloride.
- In a corrosive environment, rebars are protected as the inhibitors can be injected into the concrete as proved by the results data.
- Electro injection method of corrosion inhibiting is quite possible for horizontal structures, vertical structures, and roof structures.

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