

Evaluation of a composite corrosion inhibiting admixtures and its performance in Portland pozzolana cement

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Abstract

The effect of various inhibitive and complexing ions like hydroxide, citrate and stannate for the corrosion of steel in concrete was studied by weight loss measurements, potential–time behaviour studies, potentiodynamic polarisation studies and electrochemical impedance measurements. The salient features of these investigations were, in 100% PPC extract the passivity of steel was readily destroyed even in the presence of 10 000 ppm of chloride. However, in 100% PPC extracts containing inhibitive and complexing agents like hydroxide, citrate and stannate, the passivity of steel was maintained even in the presence of 30 000 ppm of chloride. The addition of inhibitive ions like hydroxide, citrate and stannate decreased the corrosion of steel in simulated concrete environments. Citrates, stannates and calcium oxide are very effective inhibitors for corrosion of steel in Portland pozzolana cement.

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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 an important role in decreasing the durability of concrete structures. To counteract this corrosion problem, various preventive measures such as coating to steel, coating to concrete, cathodic protection, addition of superplasticisers and corrosion inhibiting admixtures have been reported [1–5]. In PPC concrete, the competition between chloride and hydroxide ions may result in severe corrosion of embedded steel if oxygen is available for cathodic reaction [6]. Streicher studied the competitive adsorption of aggressive chloride ions in the presence of inhibitive ions [7]. ASTM specifies the use of chemical admixtures for concrete [8]. Inhibitors such as nitrites, benzoates and phosphates are studied [9,10]. Thangavel and Rengaswamy studied the effect of inhibitors in corrosion of concrete [11]. According to Treadway and Russell both sodium nitrite and to a greater extent sodium benzoate seriously reduced the strength of concrete and their use in large quantities are still questionable [12].

During the past 15 years, mainly calcium nitrite has been increasingly used. They have gained popularity for protection of reinforced and prestressed concrete structures. However, there is a considerable debate about corrosion inhibiting admixtures [13]. Apart from that, calcium nitrite is not indigenously available in India. Only imported products are large scale in use. Stannous chloride appears to be a corrosion inhibitor only for short term however it has not been suggested that it has been a good corrosion inhibitor.

Tensile strength was adversely affected by using sodium nitrite and sodium benzoate [14]. Muralidharan et al. reported that citrate- and stannate-based inhibitors are showed good performance in OPC and fly ash extracts [6]. Saraswathy et al. evaluated the composite corrosion inhibiting admixtures in OPC concrete under macrocell corrosion condition [15]. El-Jazairi et al. examined the mechanical properties of mortars produced with sodium nitrite, potassium chromate, calcium chloride and sodium benzoate [16]. Collepardi [17], Cigna et al. [18] and Nurnberger and Beul [19] cautioned about the possibility of accelerated pitting of steel reinforcement in the presence of chloride when insufficient nitrite “under dosage” is present in concrete. Recently Monticelli et al. studied more than 30 compounds as corrosion inhibitors for concrete applications [20].

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Hansson et al. also studied the principles of corrosion inhibitors in concrete [21,22].

The use of PPC in important concrete structures such as bridges, multistorey building, offshore structure, etc., are very limited due to the increased corrosion of steel in concrete. So, the suitable admixture system should be incorporated during the construction stage itself in order to avoid the corrosion of steel in concrete.

The objective of the present investigation is to design a suitable novel composite corrosion inhibiting admixture system to increase the corrosion resistance of steel embedded in concrete. The scope of present study deals with the systematic studies on the competitive role of specific inhibitors and complexing agents such as hydroxides, citrates, stannates and calcium oxide in the presence of aggressive chlorides in controlling the corrosion rate of steel in PPC extracts.

2. Experimental details

2.1. Materials

2.1.1. Cement

Portland pozzolana cement (PPC) was used throughout this investigation. The chemical composition of PPC is given below:

Oxides	PPC (%)
SiO ₂	28–32
Al ₂ O ₃	7.0–10.0
Fe ₂ O ₃	4.9–6.0
CaO	41–43
MgO	1.0–2.0
SO ₃	2.4–2.8
Loss on ignition (LOI)	3.0–3.5

2.1.2. Chemicals used

- (i) Solutions: all the solutions were prepared using distilled water.
- (ii) Inhibitors and the complexing agents:
 - (a) sodium hydroxide (AR, Fischer);
 - (b) sodium citrate (AR, Ranbaxy);
 - (c) sodium stannate (AR, Loba-chemie);
 - (d) calcium oxide (AR, Loba-chemie).

The calcium oxide was heated for a long time to decompose any calcium carbonate contained in the sample; it was then cooled and stored in a desiccator prior to use.
- (iii) Aggressive agent: sodium chloride (AR, Ranbaxy).

2.1.3. Steel

Mild steel cylindrical rod of size 6 cm length and 0.6 cm diameter was used. Mild steel rod of the following composition:

Element	Composition (%)
C	0.07
S	Nil
P	0.008
Si	Nil
Mn	0.34

and remainder iron was used throughout the experiment.

2.2. Methods

2.2.1. Preparation of PPC extracts

Portland pozzolana cement was sieved through 150 μ m sieve and extracts was prepared as follows.

To 100 g of the cement add 200 ml of distilled water and shake vigorously using a Microid flask mechanical shaker for about 1 h. The extracts were then collected by filtration. Similarly extracts for different inhibited systems (1 wt.% of cement) with various concentrations (10 000, 20 000 and 30 000 ppm) of chloride was prepared.

The systems studied were:

Plain PPC extract	Plain
Plain + NaOH	A
Plain + NaOH + sodium citrate	B
Plain + NaOH + sodium citrate + sodium stannate	C
Plain + NaOH + sodium citrate + sodium stannate + calcium oxide	D

2.2.2. pH measurements

The alkalinity of the plain PPC extract and extracts containing various inhibitors and complexing agents were measured using a digital pH meter (Model 111E, Electronics India). The pH measurements were carried out initially and subsequently upto 90 days of exposure. Initially the pH meter was calibrated using 9.2 pH buffer solutions.

2.2.3. Corrosion test setup

Mild steel rods of size 0.6 cm diameter and 6 cm length were taken for this study. The surface preparation of the steel rods were maintained uniformly for all the systems. They were given fine mechanical polishing to remove the superficial rust and subsequently polished with different grades of emery papers and finally degreased with acetone before use and these specimens were stored in a desiccator. The initial weight of the specimen was taken using Mettler balance. Triplicate mild steel specimens were tied from the hook of the glass stopper and was introduced into a PVC see-through cell containing 250 ml of the PPC extracts and PPC extracts containing different concentration of chlorides with various addition agents. The test solution was changed every week in order to induce accelerated corrosion. The temperature was maintained constant throughout these experiments at

$32 \pm 1^\circ\text{C}$. Weight losses were measured before and after immersion in test solutions at the end of exposure period of 90 days.

The corrosion rate (in mmpy) is calculated using the following equation:

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

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

2.2.4. Visual observations

During weight loss measurements, the mild steel specimens were taken out daily and carefully examined for any corrosion products like red rust observed on the surface aided with magnifying lens. The time taken for the formation of first red rust was noticed for all the systems studied. After the end of the exposure period, the specimens were removed from the test solutions and washed with water and approximate rusted area was found using a graduated scale microscope.

2.2.5. Open circuit potential (OCP) measurements

The mild steel specimens were cut in the required size. They were polished and degreased. They were dipped in the different test solutions. The open circuit potential (OCP) of the different systems were periodically monitored using a voltmeter with a high input impedance of $10\text{ M}\Omega$. Saturated calomel electrode (SCE) was used as a reference electrode. The positive terminal of the voltmeter was connected to the working electrode, i.e., mild steel rods. The common terminal was connected to the reference electrode. The corresponding potentials were recorded. OCP for all the specimens were monitored over an exposure period of 90 days. In this study, specimens in triplicate were used for each system and the average of these values were plotted against time.

2.2.6. Potentiodynamic polarisation studies

Potentiodynamic polarisation studies were carried out using mild steel specimen in PPC extracts and extracts containing different inhibitors and complexing agents with addition of 30 000 ppm of chloride. Polarisation measurements were performed to evaluate the corrosion kinetic parameters such as corrosion current (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (b_c) and anodic Tafel slope (b_a). The different test solutions were prepared using distilled water. The working electrode was a cylindrical mild steel rod embedded in araldite with an exposed area of 1 cm^2 . A rectangular platinum foil was used as the counter electrode. The area of the counter electrode is much larger than the area of the working electrode. This will exert a uniform potential field on the working electrode. Reference electrode used was SCE ($\text{Hg}/\text{HgCl}_2/\text{saturated KCl}$). A constant quantity of the test solution was taken in the polarisation cell. The working electrode was polished with

0/0, 1/0, 2/0, 3/0 and 4/0 emery papers successively and degreased with acetone. The working counter and reference electrodes were assembled and connections were made.

The test solution was continuously stirred using a magnetic stirrer to avoid the concentration polarisation. A time interval of about 10–15 min was given for each system to attain a steady state and the open circuit potential (OCP) was noted. Both cathodic and anodic polarisation curves were recorded potentiodynamically using SI 1280-B electrochemical measurement unit (Solartron, 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 conditions correspond to a potential sweep rate of 1 mV s^{-1} and potential ranges of 0.2 to -0.2 V from the OCP. Solutions were not deaerated, to make the conditions identical to the weight loss measurements. All the experiments were carried out at constant temperature of $32 \pm 1^\circ\text{C}$.

2.2.7. The ac impedance measurements

The three-electrode cell assembly was used here also. The mild steel-working electrode was polished and degreased as before and immersed in the test solution taken in the cell. The reference and the platinum counter electrodes were assembled and connections were made. A time interval of 10–15 min was given for the OCP to reach a steady value. Impedance measurements were carried out using Solartron SI 1280-B electrochemical measurement unit. The real part (Z') and the imaginary part ($-Z''$) of the cell impedance were measured for various frequencies (10 000–0.01 Hz). Plots of Z' versus $-Z''$ were made. Impedance measurements were carried out for mild steel in PPC extracts and with extracts containing different inhibited solutions with 30 000 ppm of chloride.

3. Results and discussion

3.1. pH measurements

The pH values measured for plain PPC extracts and extracts containing various inhibitors and complexing agents are given in Table 1. The pH value for plain PPC extract was 12.49. After adding inhibitors and complexing agents the initial pH ranged from 12.50 to 12.73. After the exposure period of 90 days, the pH of plain PPC extract was 8.69 and for inhibited systems ranged between 10.05 and

Table 1
pH measurements for various systems at the initial and end of exposure period of 90 days

S. no.	System	Initial pH	Final pH
1	Plain	12.49	8.69
2	A	12.50	10.05
3	B	12.71	10.12
4	C	12.71	10.13
5	D	12.73	10.16

Table 2

Corrosion rate of mild steel in plain PPC extract and extracts containing different inhibited systems with 10 000, 20 000 and 30 000 ppm of chlorides

System	First rust observed day	Area rusted (%)	Weight loss (g)	Weight gain (g)	Corrosion rate (mmpy, 1×10^{-5})
Plain	17	60	0.0505	–	2.0364
A	24	Negligible	–	0.0394	–
B	26	Nil	–	0.0408	–
C	27	Nil	–	0.0426	–
D	31	Nil	–	0.0466	–
Plain + 10 000 ppm of Cl^-	8	80	0.0519	–	2.1907
Plain + 20 000 ppm of Cl^-	7	90	0.0542	–	2.3422
Plain + 30 000 ppm of Cl^-	7	95	0.0995	–	5.1598
A + 10 000 ppm of Cl^-	12	Nil	–	0.0202	–
A + 20 000 ppm of Cl^-	10	Negligible	–	0.0115	–
A + 30 000 ppm of Cl^-	10	Negligible	–	0.0011	–
B + 10 000 ppm of Cl^-	15	Nil	–	0.0283	–
B + 20 000 ppm of Cl^-	14	Nil	–	0.0117	–
B + 30 000 ppm of Cl^-	10	Negligible	–	0.0053	–
C + 10 000 ppm of Cl^-	15	Nil	–	0.0373	–
C + 20 000 ppm of Cl^-	14	Nil	–	0.0135	–
C + 30 000 ppm of Cl^-	14	Negligible	–	0.0058	–
D + 10 000 ppm of Cl^-	16	Nil	–	0.0389	–
D + 20 000 ppm of Cl^-	15	Nil	–	0.0173	–
D + 30 000 ppm of Cl^-	15	Nil	–	0.0060	–

10.16. The pH value changed drastically for plain PPC extract. But inhibited systems maintain the pH even after 90 days of exposure in the presence of open atmosphere. This may be due to the fact that, plain PPC extract readily react with the atmosphere and gets carbonated, but action of the inhibited systems with atmosphere is very slow.

3.2. Visual observation

Visual observation for the various systems was monitored everyday upto the exposure period of 90 days are given in Table 2. The first red rust observed on the surface of steel was found to be 17 days for plain system and 31 days for system D. After adding chlorides the red rust observed was early in the period of 7 days for plain system and 10 days for inhibited systems. Even the first rust observed for all the systems, the surface layers formed by the inhibitive and complexing ions able to seal the area and stop the further promotion of rusts.

After the exposure period was over, the approximate percentage of area rusted for different system was calculated and reported in Table 2. The area rusted was 60% for plain and almost nil for the inhibited systems. After adding chlorides, the percentage of area rusted was increased in the range of 80–95% in the case of plain system. On the other hand, the inhibited systems showed almost negligible percent of area rusted (1–2%). Among all, system D showed a better performance.

3.3. Determination of self-corrosion rate by gravimetric weight loss measurements

The weight loss data for mild steel in Portland pozzolana cement extract containing different concentration of aggress-

sive ion (chloride) and various inhibitive ions and complexing agents are given in Table 2. In plain PPC extracts, the weight loss was found to be 0.0505 g after 90 days of immersion in open atmosphere. However, in the presence of chlorides the weight loss was increased by increasing the concentration of chloride from 10 000 to 30 000 ppm. An increase in the weight loss of 0.0995 g was obtained in the presence of 30 000 ppm of chlorides. On the other hand, in the presence of aggressive as well as inhibitive and complexing ions, negligible amount of weight loss was observed. Actually, weight gain was observed for the immersion period of 90 days in the open atmosphere. This is due to the fact that, inhibited and complexing systems maintaining the perfect passivity of steel even in the presence of higher concentration of aggressive ions (10 000, 20 000 and 30 000 ppm of chloride). The weight gain for the different systems follows the order: D > C > B > A.

The mechanisms of the better performance of the above systems are as follows. Inhibitive and complexing ions like hydroxide, citrate and stannate readily react with calcium ions present in the cement extracts and forms a stable and insoluble complex surface layers. The passive film integrity was tested as reported earlier [23]. The protective activity of inhibitive and complexing agents for steel in PPC extract was retained when specimens dipped in inhibited solutions transferred into fresh extracts and 3% NaCl solution without any inhibitors. This clearly shows that the inhibition is due to the formation of a stable and insoluble complex film through the process of chemisorptions on the metal surface. The film integrity was also confirmed by potential–time behaviour studies.

From the weight loss data, it was concluded that among all the systems studied, system D was more effective in

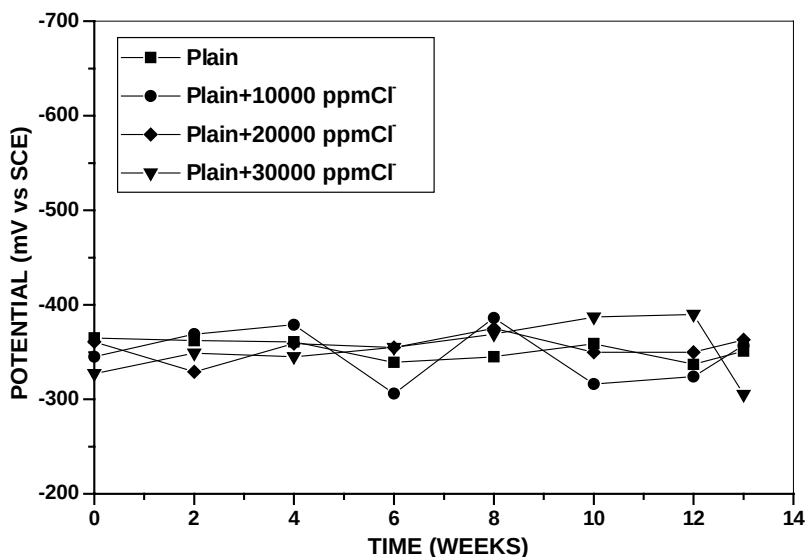


Fig. 1. Potential–time behaviour of mild steel in PPC extracts with and without chloride.

reducing the self-corrosion of steel even in the presence of 30 000 ppm of chloride.

Complex formation leads to some of the attacking anions being rendered inactive. Thus the combined effect of all the ions maintains perfect passivity on the steel surface even in the presence of higher concentration of aggressive ions.

3.4. Open circuit potential (OCP) measurements

The OCP measurements carried out for mild steel in PPC extracts and extracts containing inhibitive and complexing agents with the addition of different concentration of chlorides (10 000, 20 000 and 30 000 ppm) are shown in Figs. 1–5.

Fig. 1 relates the potential–time behaviour of plain PPC extract and extracts containing different concentration of chlorides. OCP measurements were monitored for the exposure period of 13 weeks. The plain PPC extract showed anodic potential at the end of 13 weeks. After adding chlorides, the OCP was shifted towards more anodic direction indicating the acceleration of corrosion due to chloride ions.

Fig. 2 depicts the potential–time behaviour of system A with various concentration of chlorides. It is observed from this figure that all the systems shifted the potential towards anodic direction upto 6 weeks of exposure, after that the OCP values shifted towards cathodic direction upto the exposure period of 13 weeks. The chloride added systems showed less

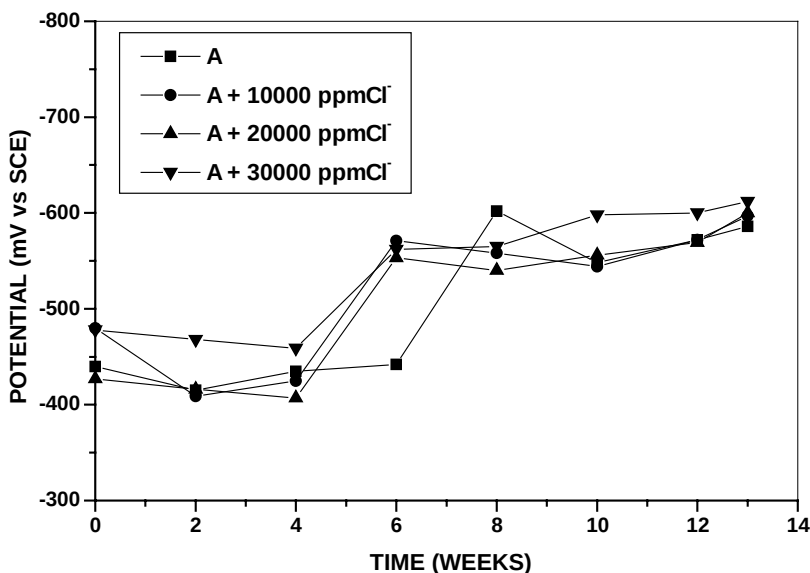


Fig. 2. Potential–time behaviour of mild steel in system A with and without chloride.

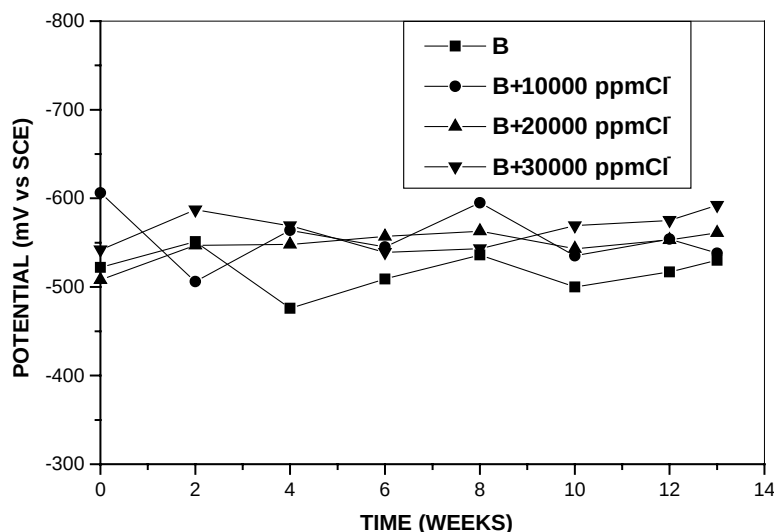


Fig. 3. Potential–time behaviour of mild steel in system B with and without chloride.

positive OCP values than respective blank systems due to the acceleration of corrosion.

Fig. 3 relates the potential–time behaviour of system B with 10 000, 20 000 and 30 000 ppm of chloride. Here, there is no change in OCP values among the various systems studied. The potential values ranged between -508 and -563 mV versus SCE.

Fig. 4 shows the potential–time behaviour of system C with and without addition of chlorides. In system C the OCP values moved towards anodic direction upto 4 weeks of exposure, afterwards there is a shift of potential towards cathodic direction upto end of exposure of 13 weeks.

Fig. 5 depicts the potential–time behaviour of system D with and without chlorides. System D shifted the potential towards cathodic direction throughout the exposure period of 13 weeks.

From the potential–time behaviour studies, it is concluded that system D was found to be the best even in 30 000 ppm of chloride indicating that perfect passivity was maintained throughout the exposure period. When any inhibitor is added to the concrete it results in a mixed inhibitor because the hydroxide ions in cement extract can be considered to act as a mild anodic inhibitor. Corrosion accelerator like chloride ions, which can occupy the defect position, competitively with hydroxide ions may induce corrosion. This observation was confirmed in the present investigations.

3.5. Potentiodynamic polarisation studies

The corrosion kinetic parameters derived from the potentiodynamic polarisation curves are given in Table 3. It is observed from Table 3 that, there is not much variation in

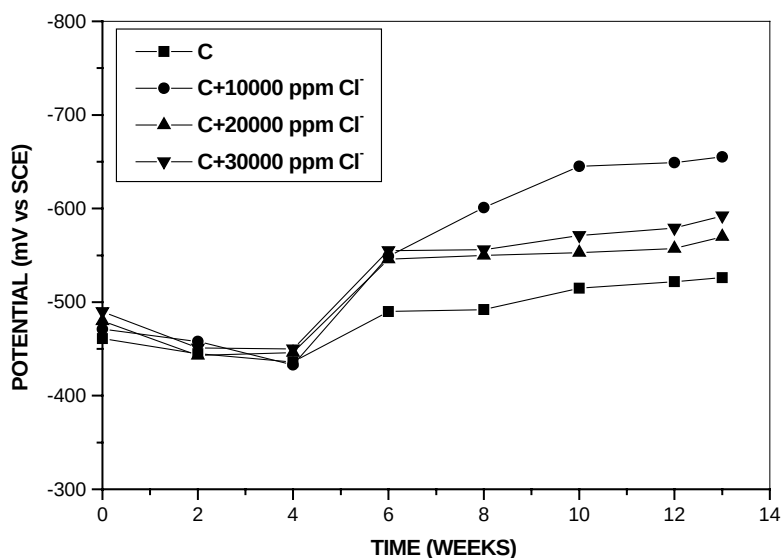


Fig. 4. Potential–time behaviour of mild steel in system C with and without chloride.

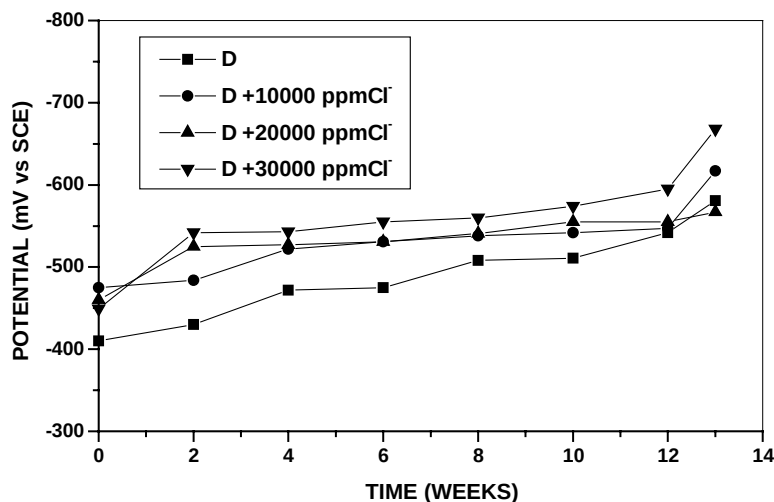


Fig. 5. Potential–time behaviour of mild steel in system D with and without chloride.

the E_{corr} values among the systems studied except system D. Plain system showed the E_{corr} value of -468 mV versus SCE. The other inhibited systems (A–C) showed slightly higher potential values when compared to plain. System D showed very high E_{corr} values of -558 mV versus SCE in 30 000 ppm of chloride. The cathodic Tafel slope (b_c) values are increasing from plain to system D, but anodic Tafel slope (b_a) values are decreasing from plain to system D. As expected, all the b_a values are higher than that of the respective b_c values. So, a definite trend is observed between cathodic and anodic Tafel slopes.

Corrosion current density value calculated using Stern–Geary equation for plain system is found to be $7.748 \mu\text{A cm}^{-2}$. After adding 30 000 ppm of chloride anions, it increases the corrosion current density to a higher value of $8.100 \mu\text{A cm}^{-2}$. On the other hand, all the inhibited systems showed less corrosion current density values when compared to plain. A corrosion current density value for system D was found to be $4.529 \mu\text{A cm}^{-2}$ even in the presence of chloride concentration of 30 000 ppm.

The corrosion rate in mmpy for plain and inhibited systems in the presence of 30 000 ppm of chloride is also reported in Table 3. The corrosion rate for plain PPC extract is found to be 0.0930 mmpy. Systems showing corrosion rate of less than 0.0930 mmpy may be considered as the

effective inhibitive systems by improving the corrosion resistance of steel in the presence of aggressive anions. After adding 30 000 ppm of chloride, the corrosion rate for plain PPC extract increased to 0.0990 mmpy. Interestingly, other inhibited systems A–D showed corrosion rate of less than 0.0930 mmpy which represent the better performance by improving the corrosion resistance of steel. Among all, system D was found to be more effective in reducing the self-corrosion of steel even in the presence of 30 000 ppm of chloride.

On the basis of potentiodynamic polarisation studies, the reduction in the corrosion rate for the different systems in 30 000 ppm of chloride follows the order: $D > C > B > A > \text{plain}$.

These results agree with the weight loss measurements and potential–time behaviour studies.

3.6. The ac impedance measurements

Impedance diagrams obtained for the frequency range 10 000–0.01 Hz at the OCP for mild steel in PPC extracts and extracts containing various inhibitors and complexing agents with addition of 30 000 ppm of chloride. Almost all the impedance Nyquist plots obtained are not perfect semi-circles and the difference has been attributed to frequency

Table 3

Potentiodynamic polarisation parameters for mild steel in plain PPC extract and extracts containing different inhibited systems with 30 000 ppm of chloride

S. no.	System	E_{corr} (mV)	Tafel slopes (mV decade ⁻¹)		I_{corr} ($\mu\text{A cm}^{-2}$)	Corrosion rate (mmpy)
			b_c	b_a		
1	Plain	−468	110	306	7.748	0.0930
2	Plain + 30 000 ppm of Cl^-	−580	115	300	8.100	0.0990
3	A + 30 000 ppm of Cl^-	−467	113	301	7.634	0.0916
4	B + 30 000 ppm of Cl^-	−469	122	292	7.212	0.0866
5	C + 30 000 ppm of Cl^-	−477	130	284	5.492	0.0659
6	D + 30 000 ppm of Cl^-	−558	135	248	4.529	0.0543

Table 4

Impedance parameters for mild steel in plain PPC extract and extracts containing different inhibited systems with 30 000 ppm of chloride

S. no.	System	OCP (mV)	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} (F cm^{-2} , 1×10^{-5})	I_{corr} ($\mu\text{A cm}^{-2}$, 1×10^{-3})	Corrosion rate (mmpy, 1×10^{-5})
1	Plain	−499	1377	35.13	50.95	61.15
2	Plain + 30 000 ppm of Cl^-	−486	745	38.14	51.00	61.05
3	A + 30 000 ppm of Cl^-	−489	1377	25.47	25.73	30.84
4	B + 30 000 ppm of Cl^-	−385	4191	8.93	8.32	9.99
5	C + 30 000 ppm of Cl^-	−397	4255	2.85	8.78	10.53
6	D + 30 000 ppm of Cl^-	−410	4745	2.83	8.16	9.79

dispersion. The R_{ct} values are calculated from the differences in impedance at lower and higher frequencies as suggested by Taib Hiakal and Haruyama [24]. These values of R_{ct} have been substituted in Stern–Geary equation to obtain the corrosion current. To obtain the C_{dl} value, the frequency at which the imaginary component of the impedance maximum ($-Z''$ max.) found and C_{dl} values are obtained from the equation:

$$C_{dl} = \frac{1}{2} \pi C_{dl} R_t$$

Table 4 gives the impedance parameters R_{ct} and C_{dl} derived from the Nyquist plots. The R_{ct} value for mild steel in plain PPC extract is found to be $1377 \Omega \text{ cm}^2$. The addition of chloride, i.e., 30 000 ppm of chloride to the plain extract drastically reduced the R_{ct} values from 1377 to $745 \Omega \text{ cm}^2$. This is due to the acceleration of corrosion by chloride anions. System A also showed a similar behaviour when compared to plain extracts. On the other hand, the inhibited systems namely B–D increased the R_{ct} values to a larger extent indicating the better performance even in the presence of higher amount of aggressive anions. Among all, system D showed the highest R_{ct} value of $4745 \Omega \text{ cm}^2$.

Similarly the C_{dl} values obtained for plain system is found to be $35 \times 10^{-5} \text{ F cm}^{-2}$. The addition of chloride anions increased the C_{dl} value to $38 \times 10^{-5} \text{ F cm}^{-2}$. System A reduced the C_{dl} value to $25 \times 10^{-5} \text{ F cm}^{-2}$, but systems B–D reduced the C_{dl} values to 8.9×10^{-5} , 2.85×10^{-5} and $2.83 \times 10^{-5} \text{ F cm}^{-2}$, respectively. It is a fact that, a good inhibited system must show a greater R_{ct} values and lesser C_{dl} values when compared to the respective blank system. In this aspect, system D was found to be more effective in controlling the corrosion rate of steel in Portland pozzolana cement even in the presence of 30 000 ppm of chloride.

Corrosion current density values obtained from Stern–Geary equations for the plain system is found to be $50.95 \times 10^{-3} \mu\text{A cm}^{-2}$. There is no appreciable change in the corrosion current density values by the addition of 30 000 ppm of chloride. System A reduced the I_{Corr} values by 50% when compared to plain but systems B–D drastically reduced the I_{Corr} values to 8.3×10^{-3} , 8.7×10^{-3} and $8.1 \times 10^{-3} \mu\text{A cm}^{-2}$, respectively, indicating their better performance in PPC extracts containing 30 000 ppm of chloride.

The corrosion rate in mmpy calculated for the different systems is also reported in Table 4. The corrosion rate for

plain and the chloride added systems showed almost a same value. As already observed in I_{Corr} values, the corrosion rate also reduced by 50% for system A. The systems B–D reduced the corrosion rate by six times when compared to plain. Among all, system D was more effective in reducing the self-corrosion of steel even in the presence of 30 000 ppm of chloride.

The reduction in the corrosion rate for different systems follows the order: $D > C > B > A > \text{plain} > (\text{plain} + \text{chloride})$. The same trend was already observed in the gravimetric weight loss measurements and potentiodynamic polarisation studies.

4. Conclusions

The following conclusions can be made on the basis of the present study:

- In plain PPC extracts, the passivity of steel was readily destroyed and the pH of the extract is affected.
- PPC extracts in the presence of chloride also suffered severe corrosion.
- PPC extracts containing inhibitive and complexing agents like hydroxides, citrate and stannate, the passivity of steel was maintained even in the presence of 30 000 ppm of chloride.
- The mechanism of action of inhibition of corrosion by these compounds is due to the formation of a stable complex film through the process of chemisorption on the metal surface.
- There is a definite correlation observed between the different techniques studied, viz. weight loss measurements, potentiodynamic polarisation studies and electrochemical impedance spectroscopy.
- The advantage of using these compounds is very effective in low concentration and there are no harmful effects by using these compounds.
- All the compounds used in these investigations are indigenously available in India.
- Citrates, stannates and calcium oxide act as very effective inhibitor for controlling the corrosion rate of steel in Portland pozzolana cement.
- Even though the studies are restricted to only cement extracts but definitely to be considered as an effective com-

posite corrosion inhibiting system for a corrosion of steel in concrete.

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References

- [1] J. Mietz, B. Isecke, *Mater. Eng.* 10 (1999) 45–59.
- [2] G. Batis, P. Pantazopoulou, A. Routoulas, *Cement Concrete Composites* 25 (3) (2003) 371–377.
- [3] H. Saricimen, M. Mohammad, A. Quddus, M. Shameem, M.S. Barry, *Cement Concrete Composites* 24 (2002) 89–100.
- [4] S.M. Trepanier, B.B. Hope, C.M. Hansson, *Cement Concrete Res.* 31 (5) (2001) 713–718.
- [5] J.M. Costa, A.D. Mercer (Eds.), *Progress in the Understanding and Prevention of Corrosion*, vol. 1, Institute of Materials, London, 1993.
- [6] S. Muralidharan, V. Saraswathy, K. Thangavel, S. Srinivasan, *J. Appl. Electrochem.* 30 (2000) 1255.
- [7] M.A. Streicher, *J. Electrochem. Soc.* 103 (1956) 375–390.
- [8] ASTM: C 494-86, *Standard Specification for Chemical Admixtures for Concrete*, pp. 248–255.
- [9] Ya. El Tantany, F.M. Al Khurah, Z. Al Fahd, *Br. Corros. J.* 19 (1984) 70.
- [10] N.S. Berke, in: V. Chaker (Ed.), *Corrosion Effect of Stray Currents and the Techniques for Evaluating Corrosion of Rebars in Concrete*, ASTM, STP 906, ASTM Publication, 1986.
- [11] K. Thangavel, N.S. Rengaswamy, *Cement Concrete Composites* 20 (1998) 283.
- [12] K.W.J. Treadway, A.D. Russell, *Inhibition of the corrosion of steel in concrete*, *Highways and Public Works (Great Britain)* 63 (1968) 1705.
- [13] P. Gu, S. Elliott, R. Hristova, J.J. Beaudoin, R. Brousseau, B. Baldock, *ACI Mater. J.* 94 (1997) 385–395.
- [14] B.B. Hope, A.K.C. Ip, *ACI Mater. J.* 86 (1989) 602–608.
- [15] V. Saraswathy, S. Muralidharan, R.M. Kalyanasundram, K. Thangavel, S. Srinivasan, *Cement Concrete Res.* 31 (2001) 789–794.
- [16] B. El-Jazairi, N.S. Berke, W.R. Grace, *The use of calcium nitrite as a corrosion inhibiting admixture to steel reinforcement in concrete*, in: C.L. Page, K.W.J. Treadway, P.B. Bamforth (Eds.), *Corrosion of Reinforcement in Concrete*, Elsevier, London, 1990, pp. 571–585.
- [17] M. Collepardi, *Admixtures for concrete*, *RILEM Proc.* 1 (1990) 287.
- [18] R. Cigna, G. Familiari, F. Gianetti, E. Proverbio, *Influence of calcium nitrite on the reinforcement corrosion in concrete mixtures containing different cements*, in: R.N. Swamy (Ed.), *Proceedings of the International Conference, University of Sheffield*, Sheffield Academic Press, Sheffield, UK, 24–28 July 1994, pp. 878–892.
- [19] U. Nurnberger, W. Beul, *Einfluss einer Feuerverzinki und PVC-Beschichtung von Bewehrungsstählen und von Irbatoren auf die Korrosion von Stahl in gerissenem Beton*, *Werkst. und Korros.* 42 (1991) 537.
- [20] C. Monticelli, A. Frignani, G. Trabaneli, *Cement Concrete Res.* 30 (2000) 635–642.
- [21] C.M. Hansson, L. Mammoliti, B.B. Hope, *Cement Concrete Res.* 28 (1998) 1775–1781.
- [22] C.M. Hansson, L. Mammoliti, B.B. Hope, *Cement Concrete Res.* 29 (1999) 1583–1589.
- [23] S. Rengamani, S. Muralidharan, M. Anbukulandainathan, S.V.K. Iyer, *J. Appl. Electrochem.* 24 (1994) 355.
- [24] F. Taib Hiakal, S. Haruyama, *Corros. Sci.* 20 (1980) 587.