

Corrosion performance of steel in composite concrete system admixed with chloride and various alkaline nitrites

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Composite concrete systems consist of both binary and ternary cements were designed. The corrosion performance of steel in composite concrete systems admixed with sodium chloride (3%NaCl) and different alkaline nitrites (0.5%NO₂⁻), namely sodium nitrite (NaNO₂), potassium nitrite (KNO₂) and calcium nitrite [Ca(NO₂)₂] were studied by conducting various electrochemical and non-electrochemical techniques. Open circuit potential and weight loss measurements were carried out for 180 days of exposure. The permeability characteristics of the composite concrete systems were studied using impressed voltage technique and rapid chloride permeability test. Linear polarisation studies showed better corrosion resistance properties of steel in binary and ternary cement concrete even in the presence of 3% sodium chloride. Chloride diffusion studies revealed that the diffusion coefficient was found to be much less for (OPC+PSC) and ternary systems. Nitrites of sodium, potassium and calcium act as anodic inhibitors and they compete with chloride ions for the ferrous ions at the steel surface to form a film of ferric oxide. Ternary systems and (OPC+PSC) performed better even in the presence of a higher amount of aggressive chloride ions. The reduction in the corrosion rate of steel in composite concrete systems follows the order: (OPC + PPC + PSC) > (OPC + PSC) > (OPC + PPC) > (PPC + PSC).

Keywords: Composite cements, Alkaline nitrites, Reinforcement corrosion, Chloride test, Admixtures

Introduction

Reinforcement corrosion is one of the major factors influencing deterioration of reinforced concrete structures. Steel embedded in concrete is normally in a passive state owing to the formation of thin iron oxide layer on the steel surface, which remains stable even in the highly alkaline environment of the concrete.¹ The corrosion process involves the breaking down of this protective layer, which leads to an expansion in the cross-section of the reinforcement due to the formation of high volume corrosion products. This process can lead to cracking or spalling of the concrete and a dangerous loss of structural stability. The most common cause of corrosion is the attack by chlorides in marine structures.² The initiation of corrosion of embedded steel occurs owing to the destruction of this protective film (depassivation) by the attack of chlorides on steel (seawater, de-icing salt, unwashed sea sand, chloride contaminated admixtures, etc.) and by the carbonation of the cover concrete due to the reaction with carbon

dioxide. This causes a reduction in the alkalinity of the concrete. The use of corrosion inhibitors may be a good alternative to other protective methods or classical repair methods, because of its lower cost and easy application.³⁻⁷ In recent years different types of corrosion inhibitors have been used in rehabilitation techniques applied to reinforced concrete structures suffering from corrosion.⁸ The effectiveness of using calcium nitrite as an inhibitor on the corrosion rate of steel embedded in concrete is well established.⁹⁻¹¹ Nitrite has shown a perfect compatibility with concrete as well as its effectiveness in chloride contaminated^{12,13} and carbonated¹⁴⁻¹⁷ concretes. In addition, mineral admixtures such as fly ash, silica fume and slag were also used as supplementary cementitious material for concrete.¹⁸⁻²⁰ Ternary blended cements were designed using high and low calcium fly ashes with an idea that beneficial aspects of the one type of ash could compensate for the shortcomings of the other.²¹ Ternary blended cements were designed using fly ash, blast furnace slag at replacement levels of 25, 50 and 70%. In addition, 10% silica fume was added. The AASHTO's rapid chloride permeability test (RCPT) and the University of Cape Town chloride conduction test were carried out to study the permeability characteristics of binary and ternary blends of 25% fly ash and 10% silica fume which exhibited significant decrease in charge passed compared

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to 25% fly ash. It has been clearly seen that the inclusion of silica fume positively contributes to reduce the permeability of concrete to chloride ions. The description of the matrix brought about by the pozzolanic reaction of silica fume, blocks the pores and results in reducing the permeability.²² Binary and ternary blended cements were formulated using Portland cement (PC), metakaolin (MK) and fly ash (PFA). Their effect on the rate of heat evolution during hydration and the heat of hydration were studied. The heat of evolution results within the first hour of hydration is possibly due to MK's high water demand whereas PFA appears to enhance PC hydration by making more water available for hydration of the PC. When combining MK and PFA in ternary PC–MK–PFA blends the MK has a dominant influence on the heat output versus time profiles.²³ Use of binary and ternary blended cements in high strength concrete was also studied.²⁴ However a systematic and detailed studies on the inhibitive performance of alkaline nitrites such as sodium, potassium and calcium nitrites on the corrosion of steel in composite cement concrete admixed with 3% sodium chloride have not yet been studied. The present investigation directed towards the studies on the inhibitive performance of different nitrites on steel in composite cement concrete admixed with 3% sodium chloride using various electrochemical and non-electrochemical techniques.

Experimental

Materials

Ordinary Portland cement (OPC, IS:8112-89), Portland pozzolana cement [PPC, IS:1489 (part 1) 1991 – fly ash based] and Portland slag cement (PSC, IS:455-1989) were used throughout this investigation. The chemical composition of OPC, PPC and PSC is given in Table 1.

Chemicals

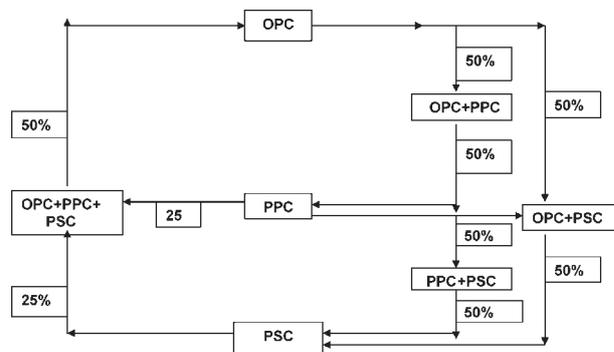
Both NaNO_2 and KNO_2 (analytical reagents, extra pure 98%) procured from Reidel Research Lab Chemicals (India) and $\text{Ca}(\text{NO}_2)_2$ imported from Russia were used. NaCl (analytical reagent, 99.5% pure) was used as aggressive agent. The inhibitors (0.5%) and corrosive agent NaCl (3%) were added to the concrete on the basis of weight of cement during mixing.

Composite systems

Composite binary and ternary cement systems such as (OPC + PSC), (OPC + PPC), (PPC + PSC) and (OPC + PPC + PSC) were used. The proportionate weight of the individual component is thoroughly mixed with other component using a roller mixer. The flow chart for making composite cements is given in Fig. 1.

Table 1 Chemical composition of OPC, PPC and PSC

Compound	OPC, %	PPC, %	PSC, %
SiO_2	20–21	28–32	26–30
Al_2O_3	5.2–5.6	7.0–10.0	9.0–11.0
Fe_2O_3	4.4–4.8	4.9–6.0	2.5–3.0
CaO	62–63	41–43	44–46
MgO	0.5–0.7	1.0–2.0	3.5–4.0
SO_3	2.4–2.8	2.4–2.8	2.4–2.8
Loss on ignition	1.5–2.5	3.0–3.5	1.5–2.5



1 Flow chart for preparation of binary and ternary cements

Methods

Compressive strength test

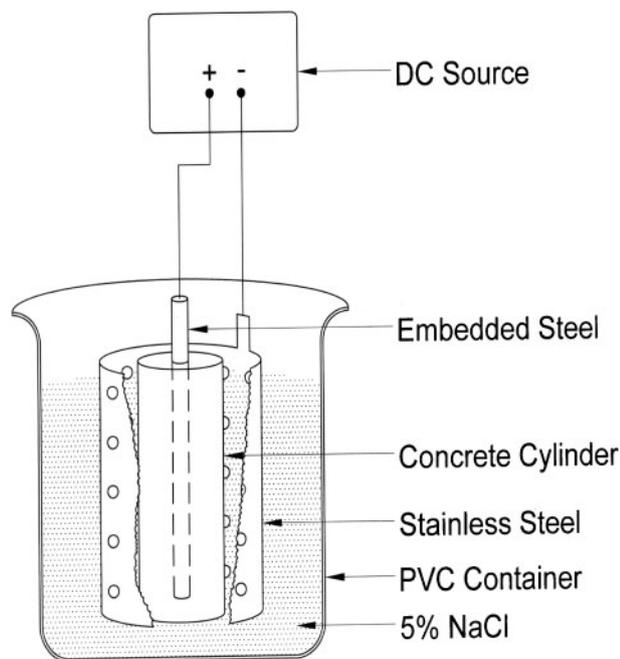
Compressive strength test was carried out²⁵ as per IS 516:1959 in concrete cubes of $150 \times 150 \times 150$ mm using 1:1.8:3.69 mix with W/C ratio of 0.55 using (OPC + PPC), (OPC + PSC), (PPC + PSC) and (OPC + PPC + PSC) with and without nitrites admixed with 3% sodium chloride. During casting, the moulds were mechanically vibrated. After 24 h, the specimens were removed from the mould and subjected to water curing for 28 days. After a specified period of curing, the specimens were tested for compressive strength using AIMIL compression testing machine at a rate of loading of $140 \text{ kg cm}^{-2} \text{ min}^{-1}$. The tests were carried out on triplicate specimens and the average compressive strength values were recorded.

Open circuit potential (OCP) measurements

Cylindrical concrete specimens of size 50 mm diameter and 60 mm height were cast with 12 mm diameter and 40 mm length thermomechanically treated (TMT) rebar were embedded in the centre of the concrete specimen with a bottom cover of 20 mm. The rebars were cleaned with pickling acid and degreased before being embedded in concrete. The concrete specimens admixed with 3% sodium chloride were cast with and without inhibitors (0.5% nitrites) in order to accelerate reinforcement corrosion. All the triplicate specimens were cured in distilled water for 28 days. After 28 days of curing, the specimens were taken out, dried and subjected to alternate wetting and drying in distilled water. One cycle consists of three days immersion in water and three days drying in open atmosphere. Measurements of OCP were made 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 (rebar) and the common terminal was connected to the reference electrode. Open circuit potential was measured in three different locations very near to the rebar and the average potentials were recorded. The cycle is continued for 180 days (30 cycles) and the potential vs. time plot is drawn using the average potentials obtained.

Impressed voltage test

The impressed voltage test has been conducted as an accelerated corrosion testing technique for comparing different characteristics of concrete.²⁶ Reinforced



2 Schematic representation of impressed voltage test

(12 mm diameter and 40 mm length TMT rebar) cylindrical concrete (50 mm diameter and 60 mm height) were cast with and without various nitrites (0.5%). Figure 2 is the schematic representation of impressed voltage test. In this technique, the concrete specimen is immersed in 5% NaCl solution and embedded steel in concrete is made anode with respect to an external stainless steel electrode serving as cathode by applying a constant positive potential of 12 V to the system from a dc source. The variation of current is recorded with time. A sharp rise in current indicates the onset of corrosion and cracking of the concrete is usually visible thereafter. The time taken for initiation of first crack can be considered as a measure of their relative resistance against chloride permeability and reinforcement corrosion.

Linear polarisation resistance (LPR) technique

Linear polarisation measurements were conducted using ACM field machine (UK). Reinforced (12 mm diameter and 40 mm length TMT rebar) cylindrical concrete (50 mm diameter and 60 mm height) admixed with 3% chloride were cast with and without various nitrites (0.5%). The experimental set-up consists of three-electrode cell assembly in which rebar acts as a working electrode, perforated stainless steel cylindrical sheet as a counter electrode and SCE as a reference electrode and the whole assembly is immersed in a beaker containing distilled water as electrolyte.

In this investigation, the rebar was polarised to the potential range of -20 to $+20$ mV from OCP at a scan rate of 0.1 mV s^{-1} and a current response was measured. The polarisation resistance R_p of the embedded steel in concrete was obtained from the slope of the potential current curve. From the R_p values, the corrosion current I_{corr} ($\mu\text{A cm}^{-2}$) and corrosion rate were determined using the following relationship²⁷

$$I_{\text{corr}} = B/R_p \quad (1)$$

where B is a Stern–Geary constant = 26 mV.

From the I_{corr} value, the corrosion rate (mm/year) was calculated as

$$\text{Corrosion rate} = 0.0116 I_{\text{corr}}$$

All the experiments were carried out at a room temperature of $35 \pm 1^\circ\text{C}$.

Gravimetric weight loss measurement

Reinforced (12 mm diameter and 40 mm length TMT rebar) cylindrical concrete (50 mm diameter and 60 mm height) admixed with 3% chloride were cast with and without various nitrites (0.5%). The initial weight of the rebar samples was taken in 4-digit electronic balance for gravimetric weight loss measurements. After the curing period was over, all the specimens were completely immersed in distilled water. The specimens were maintained in the same condition for three days and then subjected to drying for another three days. Therefore, one alternate wetting and drying cycle consists of three days' immersion in water and three days' drying in open air at room temperature. All the concrete specimens were subjected to 30 complete cycles. Tests were conducted on a minimum of three replicate specimens and the average values were reported. The corrosion rate was assessed from the difference in weight loss values between initial and final exposure period. The corrosion rate²⁸ is calculated using the following equation

$$\text{Corrosion rate} = \frac{87.6 W}{DAT} \quad (2)$$

where W is the weight loss (mg), D is the density of the material used (g cm^{-3}), T is the time duration (h) and A is the area of the specimen (cm^2)

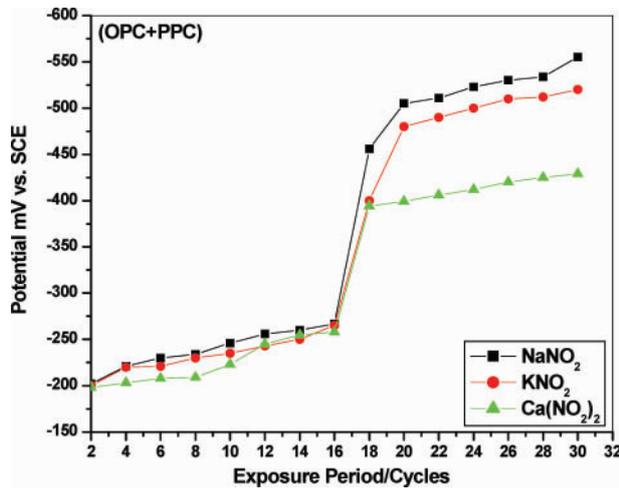
Rapid chloride permeability test

The resistance to chloride ion penetration in terms of total charge passed in coulombs through concrete specimens was measured as per ASTM C1202. Rapid chloride permeability test were conducted on binary and ternary concrete system with and without 0.5% $\text{Ca}(\text{NO}_2)_2$. Concrete disc of 95 mm diameter and 50 mm thickness were cast and allowed to cure for 28 days. After completion of curing period the concrete specimens were subjected to RCPT by impressing 60 V.

Two halves of the specimens are sealed with PVC container of diameter 90 mm. One side of the container is filled with 3% NaCl solution (that side of the cell will be connected to the negative terminal of the power supply), and the other side is filled with 0.3 N NaOH solution (which will be connected to the positive terminal of the power supply). Current is measured at every 30 min up to 6 h. Chloride contamination and temperature at every 30 min was also monitored. From the data of current and time, chloride permeability is calculated in terms of coulombs at the end of 6 h. The total charge passed is a measure of the electrical conductance of the concrete during the period of the test.

Chloride diffusion coefficient

The amount of chloride ion migrating through various concretes was monitored periodically by removing small aliquots and determining the chloride concentration of these samples until steady state was reached (120 h). Chloride diffusion coefficients were calculated using Nernst–Einstein equation.^{29,30}



3 Potential v. time curve for rebar in (OPC+PPC) concrete with different nitrites mixed with 3%Cl⁻

$$D = \frac{JRTL}{ZFC_0E} \quad (3)$$

where *D* is the chloride diffusion coefficient (cm² s⁻¹), *J* is the flux of chloride ions (mol cm⁻² s⁻¹), *R* is the gas constant (8.314 J K⁻¹ mol⁻¹), *T* is the absolute temperature (K), *L* is the thickness of the specimen (cm), *Z* is the valency of chloride ion (*Z*=1), *F* is the Faradays constant (9.648 × 10⁴ J V⁻¹ mol⁻¹), *C*₀ is the initial chloride ion concentration (mol L⁻¹) and *E* is the potential applied (60 V)

pH measurement and free chloride estimation

The pH of both binary and ternary concrete extracts was determined using a portable Roy Instrument (model pH 300) pH meter which was calibrated using a buffer solution of pH 9. pH values were measured at the end of an exposure period of 180 days.

At the end of the exposure period, concrete specimens were split open and the concrete core sample very near to the rebar was taken, powdered and the fine powder was taken for chloride analysis. The extract prepared from the powdered sample was then analysed for free chloride contents as per the procedures reported elsewhere.³¹ About 20 cm³ of filtered solution was taken and the free chloride content was estimated by standard silver nitrate solution using potassium chromate as an indicator. Titrations are repeated until the concordant values were obtained. The amount of free chloride content calculated was expressed in terms of parts per million (ppm) on the basis of weight of sample taken for analysis.

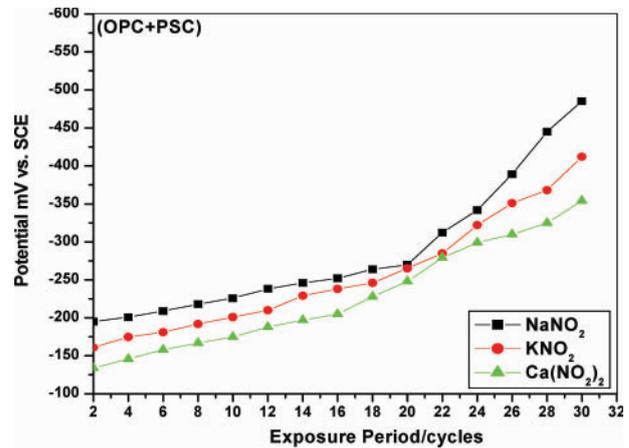
Visual observations

At the end of the test period of 180 days, the concrete specimens were split open and the rebars were taken out and visually examined for any corrosion products like red rust observed on the surface aided with magnifying lens and the percentage of area rusted for each system was recorded.

Results and discussion

Compressive strength of concrete

Table 2 shows the 28 days compressive strength of (OPC+PPC), (OPC+PSC), (PPC+PSC) and (OPC+PPC+PSC) composite systems admixed with 3%



4 Potential v. time curves for rebar in (OPC+PSC) concrete with different nitrites mixed with 3%Cl⁻

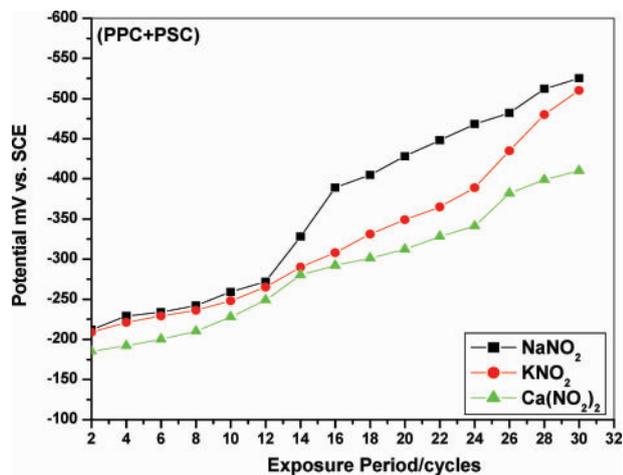
chloride and with and without nitrites. The compressive strength values obtained for (OPC+PPC), (OPC+PSC) and (PPC+PSC) binary systems were found to be 29.30, 31.75 and 28.23 MPa respectively. The ternary system (OPC+PPC+PSC) showed compressive strength value of 32.10 MPa. These results indicated that compared to binary system, ternary system showed a slight increase in compressive strength. Addition of nitrite inhibitor (0.5%) does not affect the compressive strength values. For example in the case of ternary system the compressive strength values were 32.10, 32.20 and 32.25 MPa respectively for sodium, potassium and calcium nitrites added concrete respectively. These results indicated that addition of inhibitors did not affect the mechanical properties of the concrete.

Open circuit potential measurements

The threshold potential for steel in concrete is reported by various authors.^{32,33} Potentiometric determination of chloride threshold values for rebar depassivation experimental and statistical study was reported by Izquierdo *et al.*³⁴ Open circuit potential measurements made on different binary and ternary systems with different alkaline nitrites are given in Figs. 3–6. From these figures, it was inferred that steel embedded in binary

Table 2 Compressive strength for various composite concrete system admixed with 3% chloride and various nitrites

System	Inhibitor	Average compressive strength at 28 days, MPa
OPC+PPC	Control	29.30
	NaNO ₂	29.57
	KNO ₂	29.70
	Ca(NO ₂) ₂	29.72
OPC+PSC	Control	31.75
	NaNO ₂	31.80
	KNO ₂	31.82
	Ca(NO ₂) ₂	31.85
PPC+PSC	Control	28.23
	NaNO ₂	28.30
	KNO ₂	28.50
	Ca(NO ₂) ₂	28.50
OPC+PPC+PSC	Control	32.10
	NaNO ₂	32.10
	KNO ₂	32.20
	Ca(NO ₂) ₂	32.25



5 Potential v. time curves for rebar in (PPC+PSC) concrete with different nitrites mixed with 3%Cl⁻

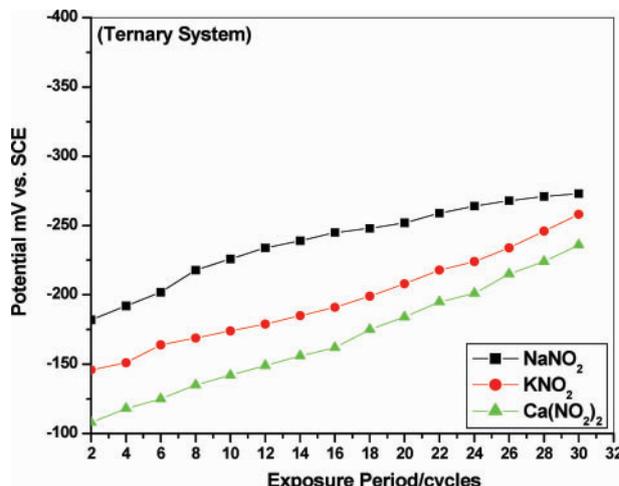
system showed active condition (high negative potential) at the end of 16, 20 and 12 cycles of exposure for (OPC+PPC), (OPC+PSC) and (PPC+PSC) respectively. On the other hand, steel embedded in ternary system showed passive condition (less negative potential) throughout the exposure period of 30 cycles. These results illustrated that almost all the nitrites behave similarly in binary and ternary systems. Compared to the binary system, ternary system maintain their passivity of steel even after 30 cycles of exposure period indicating their better performance in 3% chloride admixed concrete. Among the nitrites studied, Ca(NO₂)₂ showed less negative potential than other nitrites.

Impressed voltage test

From the Table 3, it was observed that the maximum anodic current measured were found to be 38, 27 and 45 mA for the binary systems (OPC+PPC), (OPC+PSC) and (PPC+PSC) respectively. On the other hand, the ternary system showed 25 mA. The time taken for initial crack also revealed three, four and two days for binary systems where as the ternary system showed nine

Table 3 Impressed voltage test parameters for steel in composite concrete system admixed with 3% chloride and various nitrites

System	Inhibitor	Maximum anodic current, mA	Time to initiation of cracking, days
OPC+PPC	Control	38	3
	NaNO ₂	31	4
	KNO ₂	29	6
	Ca(NO ₂) ₂	26	9
OPC+PSC	Control	27	4
	NaNO ₂	25	6
	KNO ₂	20	10
	Ca(NO ₂) ₂	19	12
PPC+PSC	Control	45	2
	NaNO ₂	35	3
	KNO ₂	32	5
	Ca(NO ₂) ₂	29	7
OPC+PPC+PSC	Control	25	9
	NaNO ₂	12	12
	KNO ₂	10	15
	Ca(NO ₂) ₂	10	18



6 Potential v. time curves for rebar in (OPC+PPC+PSC) concrete with different nitrites mixed with 3%Cl⁻

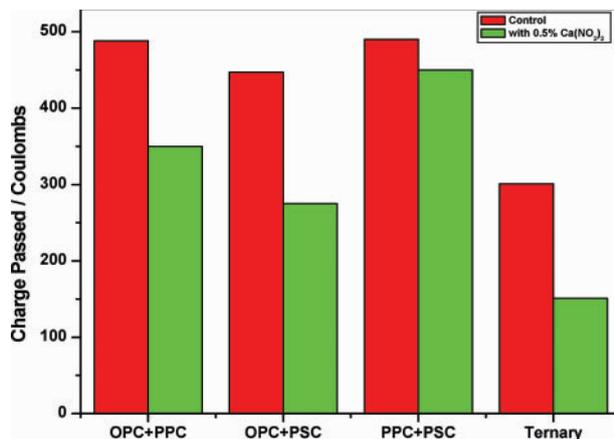
days. These data confirmed the fact that in ternary system, the increased formation of C-S-H gel and pore filling effect reduced the anodic current measured. Hence the time taken for initial crack was enhanced. The addition of nitrite inhibitors considerably reduced the anodic current flow, as a result the time taken for initial crack enhanced to a greater extent. Among the nitrite systems studied, Ca(NO₂)₂ showed the better efficiency in reducing the corrosion rate of steel in binary as well as in ternary system. For example, in the case of (OPC+PSC) system, the time taken for initial crack measured were found to be 6, 10 and 12 days for NaNO₂, KNO₂ and Ca(NO₂)₂ added concrete respectively. On the basis of maximum anodic current flow measured, the efficiency of the nitrites in reducing the corrosion rate of embedded steel follows the order Ca(NO₂)₂>KNO₂>NaNO₂. On the basis of time taken for initial crack, the efficiency of the system in reducing the corrosion rate of embedded steel follows the order: ternary>binary.

Linear polarisation resistance studies

From the Table 4, it was observed that among the binary systems studied, (OPC+PSC) showed the lowest

Table 4 Corrosion rate obtained from LPR method for composite concrete systems mixed with 3% chloride with various nitrites

System	Inhibitor	Corrosion rate, mm/year
OPC+PPC	Control	0.0088
	NaNO ₂	0.0082
	KNO ₂	0.0071
	Ca(NO ₂) ₂	0.0070
OPC+PSC	Control	0.0063
	NaNO ₂	0.0083
	KNO ₂	0.0048
	Ca(NO ₂) ₂	0.0044
PPC+PSC	Control	0.0998
	NaNO ₂	0.0661
	KNO ₂	0.0557
	Ca(NO ₂) ₂	0.0111
OPC+PPC+PSC	Control	0.0071
	NaNO ₂	0.0022
	KNO ₂	0.0014
	Ca(NO ₂) ₂	0.0012



7 Quantity of charge passed for various composite system with Ca(NO₂)₂ admixed with 3%Cl⁻

corrosion rate and (PPC+PSC) showed higher corrosion rate. For example (PPC+PSC) system showed corrosion rate of 0.0998, 0.0661, 0.0557 and 0.0111 mm/year for control, NaNO₂, KNO₂ and Ca(NO₂)₂ added concrete respectively. On the other hand (OPC+PSC) system reduced the corrosion rate to 10 times than (PPC+PSC) system.

In the case of ternary system, the corrosion rate of steel was 0.0071, 0.0022, 0.0014 and 0.0012 mm/year for control, NaNO₂, KNO₂ (CaNO₂)₂ added concrete respectively. When compared to the binary system, ternary system showed least corrosion rate in 3% chloride admixed concrete and with and without 0.5% nitrites.

On the basis of efficiency of alkali nitrites to reduce the corrosion rate of steel in binary and ternary systems follows the order



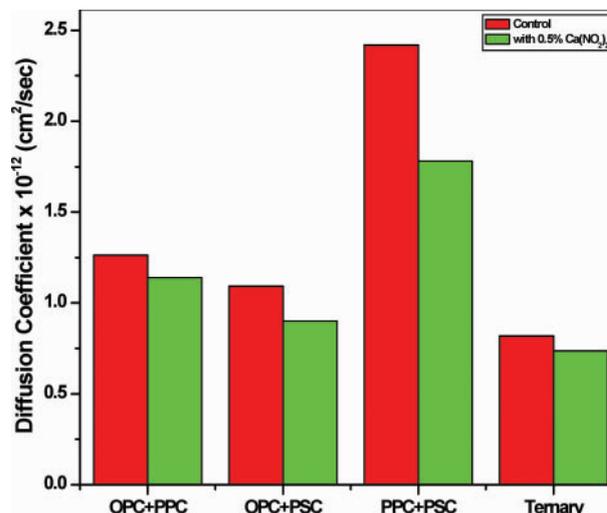
The reduction in the corrosion rate by the composite systems follows the order



Rapid chloride permeability test

Figure 7 shows the quantity of charge passed in coulombs calculated from RCPT for different combinations of binary and ternary systems. From the chart, it was observed that the quantity of charge passed was found to be 488, 447, 490 and 301 C for (OPC+PPC), (OPC+PSC), (PPC+PSC) and (OPC+PPC+PSC) systems respectively. Among all, (PPC+PSC) showed higher coulomb value and ternary showed the least coulomb value, i.e. when compared to (PPC+PSC) system, the ternary system is found to have 1.6 fold decrease in coulomb value. This reduction in coulomb may be observed due to the pore structure refinement in ternary system. The pore structure refinement in the ternary system is achieved through fineness of the materials namely OPC (295 m² kg⁻¹), PPC (363 m² kg⁻¹) and PSC (385 m² kg⁻¹). The fineness of the ternary system may be in the range between 295 and 385 m² kg⁻¹.

The addition of 0.5% Ca(NO₂)₂ considerably reduced the coulomb value in binary and ternary systems studied. For example, 301 C was measured for the (OPC+PPC+PSC) system. Addition of 0.5% Ca(NO₂)₂



8 Chloride diffusion coefficient for various composite systems with Ca(NO₂)₂ admixed with 3%Cl⁻

reduced the charged passed to 151 C. The combination of ternary system with Ca(NO₂)₂ showed superior impermeability characteristics due to improved C-S-H gel structure. The RCPT results also confirmed the fact that the porosity was reduced in ternary system when compared to binary system studied.

Chloride diffusion coefficient

Figure 8 represents the steady state diffusion coefficients over a period of 120 h for different combinations of binary and ternary cements.

The chloride diffusion coefficient (CDC) calculated for various systems indicated that ternary system showed the least value when compared to binary systems. The increased pore structure reinforcement in ternary system reduced the chloride diffusion rate. Moreover the high Al₂O₃ content in PSC reacts with chloride to form Friedel's salt. The formation of such compounds also reduced the porosity. The addition of 0.5% Ca(NO₂)₂ considerably reduced the chloride diffusion coefficient in binary and ternary systems studied. For example CDC of $2.42 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ was measured for the (PPC+PSC) system. Addition of 0.5% Ca(NO₂)₂ reduced the chloride diffusion coefficient to $1.78 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$. Ternary system showed the least chloride diffusion coefficient, indicating their better pore structure refinement in concrete.

Gravimetric weight loss measurements

The weight loss data for steel in binary and ternary systems admixed with 3% chloride and with and without nitrites are given in Table 5.

It was observed from the table that among the binary system, (OPC+PSC) showed the least corrosion rate than others. The corrosion rate for (OPC+PSC) system was found to be 0.0075, 0.0069, 0.0063 and 0.0062 mm/year for control, NaNO₂, KNO₂ and Ca(NO₂)₂ respectively. As observed earlier in LPR studies a 10 fold decrease in the corrosion rate values for the (OPC+PSC) system observed when compared to (PPC+PSC) system.

Ternary system showed corrosion rate values of 0.0057, 0.0056, 0.0045 and 0.0026 mm/year for control, NaNO₂, KNO₂ and Ca(NO₂)₂ respectively. On the basis of efficiency of alkali nitrites to reduce the corrosion rate

Table 5 Corrosion rate obtained from weight loss method for composite concrete systems admixed with 3% chloride with various nitrites

System	Inhibitor	Corrosion rate, mm/year	pH	Free chloride, ppm	Area rusted, %
OPC+PPC	Control	0.0112	12.55	2838	100
	NaNO ₂	0.0089	12.57	2833	80
	KNO ₂	0.0079	12.57	2625	75
	Ca(NO ₂) ₂	0.0078	12.58	2600	70
OPC+PSC	Control	0.0075	12.60	2580	95
	NaNO ₂	0.0069	12.62	2400	75
	KNO ₂	0.0063	12.62	2370	70
	Ca(NO ₂) ₂	0.0062	12.63	2300	65
PPC+PSC	Control	0.1049	12.37	3660	100
	NaNO ₂	0.0875	12.44	3250	85
	KNO ₂	0.0734	12.45	2900	80
	Ca(NO ₂) ₂	0.0616	12.48	2800	75
OPC+PPC+PSC	Control	0.0057	12.70	2000	90
	NaNO ₂	0.0056	12.70	1970	70
	KNO ₂	0.0045	12.71	1718	65
	Ca(NO ₂) ₂	0.0026	12.72	1700	60

of steel in binary and ternary systems follows the order



The reduction in the corrosion rate by the composite systems follows the order



The better performance of Ca(NO₂)₂ than the KNO₂ and NaNO₂ may be due to the difference in the solubility factor among them. The solubility of calcium nitrite is comparatively lesser than potassium and sodium nitrites. Hence the probable leaching of inhibitor from the concrete is less for calcium nitrite. So calcium nitrite remains long time in the concrete and gives perfect protection to the steel rebar.

pH and free chloride estimation

Table 5 represents the alkalinity and free chloride estimation of different binary and ternary systems after 180 days of exposure. It was found that there is a slight reduction in alkalinity found in (PPC+PSC) system when compared to the other binary and ternary systems. This is due to the fact that PPC has 25% replacement of fly ash and PSC has 55% replacement of slag which induced reduction in OH⁻ ions and hence reduced the alkalinity.

Free chloride estimated for different binary and ternary systems was given in Table 5. Ternary system showed the lowest free chloride contents. With the result, the lowest corrosion rate observed for ternary system from weight loss and LPR techniques.

Visual observation

Table 5 represents the corroded area of the rebar after 180 days of exposure in binary and ternary systems. From the table, it was noted that both binary (OPC+PSC) and ternary (OPC+PPC+PSC) systems are found to have lesser corroded area than the other systems. When compared to the binary and ternary, ternary system performed well due to the fact that the blended cements refined the pore structure and hence reduced the permeability of concrete and corrosion of embedded rebars.

Conclusions

Ternary system showed higher compressive strength compared to binary system. Addition of nitrites (0.5%)

did not affect the strength properties. Open circuit potential measurements illustrated that ternary system maintain their passivity of steel even after 30 cycles of exposure period whereas binary system showed active condition at the end of 16, 20 and 12 cycles of exposure for (OPC+PPC), (OPC+PSC) and (PPC+PSC) respectively. Among the nitrites studied Ca(NO₂)₂ showed less negative potential than other nitrites. Impressed voltage test results indicated that the maximum anodic current measured were found to be 38, 27 and 45 mA for the binary systems studied. On the other hand a ternary system showed 25 mA only. This inferred that the efficiency of the system in reducing the corrosion rate of embedded steel follows the order: ternary>binary. Studies of LPR indicated that (OPC+PSC) reduced the corrosion rate by 10 times when compared to (PPC+PSC). Composite systems reduced the corrosion rate of embedded steel as follows: ternary>OPC+PSC>OPC+PPC>PPC+PSC. RCPT test results showed a 1.6 fold decrease in coulombs value for the ternary system when compared to binary system. This reduction in coulombs may be observed due to the improved pore structure refinement in the ternary system. Gravimetric weigh loss measurements also showed a 10 fold decrease in corrosion rate of embedded steel for OPC+PSC system when compared to PPC+PSC system. The high Al₂O₃ content in PSC reacts with chloride and forms Friedels salts. The formation of such complexes considerably reduced the porosity and corrosion rate of embedded steel.

Acknowledgements

The authors thank the Director, CECRI, Karaikudi for his kind permission to publish this article. The authors also gratefully acknowledge the support from Center for Concrete Corea, South Korea for financial assistance.

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