

**Effect of Cation Type of Chloride Salts, and Sulfate Ion on
Chloride Diffusion, Chloride Binding and Rebar Corrosion in
Concrete Containing Corrosion Inhibitors**

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By

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Dedicated to

My parents,

Late Hareswar Das

(Father)

&

Anu Das

(Mother)



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CERTIFICATE

It is certified that the work contained in the thesis entitled “**Effect of cation type of chloride salts, and sulfate ion on chloride diffusion, chloride binding and rebar corrosion in concrete containing corrosion inhibitors**” submitted by **Mr. Jyotish Kumar Das (Roll No. 146104021)** to the Indian Institute of Technology Guwahati for the award of the degree of **Doctor of Philosophy** has been carried out under my supervision in the Department of Civil Engineering, Indian Institute of Technology Guwahati. This work has not been submitted elsewhere for the award of any other degree or diploma.

Place: IIT Guwahati

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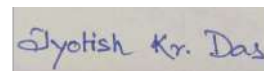
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ABSTRACT

Corrosion damage of steel reinforcement embedded in concrete is one of the major factors that affects the durability and decreases the service life of reinforced concrete structures, which results in huge economic losses. Corrosion of steel reinforcement can be initiated as a consequence of chloride contamination and/or carbonation of concrete. Chloride ions are the primary cause for corrosion of steel reinforcement that leads to the deterioration and failure of reinforced concrete structures exposed to chloride-laden environment. The ingress of chloride ions into the concrete exposed to salt lakes, de-icing salts, and marine environment results in depassivation of the steel bars embedded in concrete. The cation type of chloride salts plays a major role in the process of chloride ingress, chloride binding, and steel reinforcement corrosion in concrete. Further, sulfate ions also exist concomitantly with chloride ions in saline and marine environment. The reaction of sulfate ions with cement hydrates results in the formation of expansive products namely ettringite, gypsum, and magnesium hydroxide in concrete. These expansive products cause microcracks in the hardened cement paste, which provide additional transport channels into the concrete for penetration of aggressive ions. Due to huge repair costs for the corrosion damages in reinforced concrete structures, it is essential to effectively minimize the corrosion damage of reinforced concrete structures exposed to aggressive environment. A wide range of methods namely cathodic protection, protective coatings and sealers, re-alkalization of concrete, chloride extraction and use of corrosion inhibitors, etc. have been used to prevent corrosion of steel reinforcement, thereby improving the durability of reinforced concrete structures. Among them, use of corrosion inhibitors is proved to be the long term efficient method to prevent corrosion of steel reinforcement due to several benefits such as convenience, cost-effectiveness, easy availability and high resistance to corrosion.

The present research work investigates the effect of cation type of chloride salts and corrosion inhibitors on penetration of chloride ions, chloride binding, and changes in microstructure of concrete prepared from OPC and PPC, and exposed to chloride and composite chloride-sulfate solutions. Further, the effect of mix parameters and exposure condition (i.e., internal exposure and external exposure) on the performance of sodium nitrite (NaNO_2) and di-Sodium hydrogen phosphate (Na_2HPO_4) against corrosion of steel reinforcement in concrete exposed to chloride and composite chloride-sulfate environment have been investigated. For this purpose, an experimental investigation was carried out where concrete cube specimens of size 150 mm, and cylindrical reinforced concrete

specimens of size 72 mm in diameter and 300 mm in length with a centrally embedded reinforcing steel bar were prepared from ordinary Portland cement (OPC) and Portland pozzolana cement (PPC) using water-to-cement ratios (w/c) of 0.45 and 0.55. Sodium nitrite (NaNO_2) and di-Sodium hydrogen phosphate (DHP) were used as the corrosion inhibitors at the admixed dosage of 1% and 3% by weight of cement during the preparation of concrete mixes. In the present research work, sodium chloride (NaCl), magnesium chloride (MgCl_2), and calcium chloride (CaCl_2) were used as the sources of chloride ions, whereas magnesium sulfate (MgSO_4) was used as the source of sulfate ions. The concrete cube specimens were used for compressive strength test, for the preparation of concrete powder electrolyte solution (CPES), and for obtaining the chloride diffusion coefficient of concrete. The concrete powder electrolyte solution (CPES) closely represents all the species present in the concrete around the vicinity of reinforcing steel as the solution was extracted from concrete powder. The CPES was used as the electrolyte in potentiodynamic polarization test. The half-cell potential and linear polarization resistance (LPR) measurements were conducted on the cylindrical reinforced concrete specimens exposed to chloride, and composite chloride-sulfate environment. For internal chloride exposure condition, chloride salts were added to the concrete mixes during the time of preparation. For external exposure condition, the concrete specimens were subjected to chloride and composite chloride-sulfate solutions of varying concentrations for different exposure periods. The free chloride ion and total chloride ion contents of concrete were determined by potentiometric titration. The obtained chloride contents were used to determine the chloride diffusion coefficient (estimated using Fick's second law of diffusion) and chloride binding of concrete. In addition, to examine the influence of chloride salts and corrosion inhibitors on the changes in microstructure of concrete subjected to chloride and composite chloride-sulfate environment, X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and Field emission scanning electron microscope (FESEM) analyses were carried out. From the obtained XRD patterns, the weight percentage of compounds formed in concrete was estimated from semi-quantification analysis using the reference intensity ratio (RIR) matrix-flushing method.

From the obtained results, it is observed that the addition of chloride salts namely NaCl , MgCl_2 , and CaCl_2 increased the 28-day compressive strength of concrete whereas the addition of corrosion inhibitors i.e., sodium nitrite (NaNO_2) and di-Sodium hydrogen phosphate (DHP) reduced the compressive strength of concrete than control mix irrespective of cement type and w/c. The reduction in compressive strength was more

significant in case of DHP than NaNO_2 with respect to control mix. Further, the cation type associated with chloride ions greatly influenced the compressive strength of concrete and the compressive strength decreased in the order of: $\text{CaCl}_2 > \text{MgCl}_2 > \text{NaCl}$ irrespective of cement type and corrosion inhibitors.

The results of potentiodynamic polarization test indicated that for both OPC and PPC, the passivity range of reinforcing steel was higher in the concrete powder electrolyte solution (CPES) admixed with CaCl_2 as compared to MgCl_2 and NaCl , whereas in the presence of corrosion inhibitors, the steel reinforcement in the CPES admixed with NaCl showed higher passivity range as compared to CaCl_2 and MgCl_2 . The addition of corrosion inhibitors increased the passivity of reinforcing steel in the CPES admixed with chloride salts. Between the corrosion inhibitors, sodium nitrite (NaNO_2) was more effective in enhancing the passivity of steel reinforcement as compared to di-Sodium hydrogen phosphate (DHP). From the obtained results of electrochemical measurements in concrete subjected to internal chloride exposure, it is observed that the corrosion activity of steel reinforcement was lower in the concrete in the presence of internal chloride irrespective of cation type of chloride salts, and presence of corrosion inhibitors. Concrete admixed with NaCl showed more negative half-cell potential and higher corrosion current density than that admixed with CaCl_2 and MgCl_2 for both cements and corrosion inhibitors. Between MgCl_2 and CaCl_2 , initially, more negative half-cell potential and higher corrosion current density were observed in the concrete admixed with MgCl_2 as compared to CaCl_2 , whereas during later age, opposite variation in corrosion parameters was observed between MgCl_2 and CaCl_2 . Between corrosion inhibitors, sodium nitrite was more effective in decreasing the extent of corrosion of steel reinforcement as compared to DHP. The addition of NaNO_2 , and DHP increased the binding of chloride ions in concrete thereby resulting in lower amount of free chloride near steel reinforcement. Further, the OPC concrete mixes showed better performance against steel reinforcement corrosion as compared to PPC concrete mixes in the presence of internal chloride.

The cation type of chloride salts greatly affected the half-cell potential and corrosion current density of steel reinforcement in cylindrical reinforced concrete specimens exposed to chloride and composite chloride-sulfate solutions. In case of exposure to only chloride solutions, NaCl was more aggressive in depassivating the steel reinforcement early thereby reducing corrosion initiation period, and also increasing corrosion current density as compared to CaCl_2 followed by MgCl_2 . In case of concrete exposed to composite chloride-

sulfate solutions, the probability of occurrence of corrosion, and corrosion current density of steel reinforcement were higher in the concrete exposed to $\text{CaCl}_2 + \text{MgSO}_4$ solution as compared to $\text{NaCl} + \text{MgSO}_4$ solution followed by $\text{MgCl}_2 + \text{MgSO}_4$ solution. The probability of occurrence of corrosion and corrosion current density of steel reinforcement increased with increase in chloride salt concentration in the chloride exposure solutions. Addition of corrosion inhibitors enhanced the resistance of concrete against corrosion for exposure to chloride as well as composite chloride-sulfate exposure solutions. Besides, NaNO_2 exhibited improved resistance against rebar corrosion as compared to DHP even in the presence of higher amount of chloride ions near rebar level regardless of cement type and chloride salts in chloride exposure solutions. Corrosion inhibitors were comparatively more effective against corrosion of steel reinforcement in OPC concrete than PPC concrete in case of exposure to chloride as well as composite chloride-sulfate solutions. The formation of denser microstructure in PPC concrete was more dominant in minimizing the corrosion activity of steel reinforcement over the effect of corrosion inhibitors.

The results obtained from chloride diffusion study showed that the cation type of chloride salts, and admixed corrosion inhibitors i.e., NaNO_2 and DHP have significant effect on free chloride content profile, apparent chloride diffusion coefficient (D_{app}), and chloride binding capacity (R) of concrete exposed to chloride and composite chloride-sulfate solutions. The free chloride content at all depth intervals from exposure surface as well as the apparent chloride diffusion coefficient of OPC and PPC concrete admixed with and without different corrosion inhibitors, and exposed to chloride solutions decreased in the order of $\text{NaCl} > \text{CaCl}_2 > \text{MgCl}_2$, whereas the chloride binding capacity (R) decreased in the order of R: $\text{CaCl}_2 > \text{MgCl}_2 > \text{NaCl}$. In case of exposure to composite chloride-sulfate solutions, the free chloride content decreased in the order of C_F : $\text{CaCl}_2 + \text{MgSO}_4 > \text{NaCl} + \text{MgSO}_4 > \text{MgCl}_2 + \text{MgSO}_4$, and the chloride diffusion coefficient decreased in the order of D_{app} : $\text{MgCl}_2 + \text{MgSO}_4 > \text{NaCl} + \text{MgSO}_4 > \text{CaCl}_2 + \text{MgSO}_4$. Further, the chloride binding capacity (R) of concrete admixed with and without corrosion inhibitors, and exposed to composite chloride-sulfate solutions decreased in the order of R: $\text{NaCl} + \text{MgSO}_4 > \text{MgCl}_2 + \text{MgSO}_4 > \text{CaCl}_2 + \text{MgSO}_4$ for both cements. The addition of corrosion inhibitors in concrete decreased the free chloride ion content and chloride diffusion coefficient as compared to control concrete for both chloride and composite chloride-sulfate solutions. Between the corrosion inhibitors, NaNO_2 showed lower chloride diffusion coefficient than DHP for all exposure solutions. Further, in the concrete exposed to chloride solutions, DHP exhibited higher chloride binding capacity than NaNO_2 . This is due to the dominant effect of formation of

chlorapatite in the concrete containing DHP over the effect of lower extent of physical binding of chloride ions in case of NaNO_2 due to the significant effect of partial replacement of adsorbed nitrite ions from C-S-H by chloride ions. While comparing between OPC and PPC, the chloride binding capacity was higher in OPC concrete as compared to PPC concrete regardless of presence of corrosion inhibitors, w/c and cation type of chloride salt in both chloride and composite chloride-sulfate solutions. However, PPC concrete showed lower chloride diffusion coefficient as compared to OPC concrete. The formation of various compounds in the concrete as indicated by the XRD patterns were corroborated with the FTIR spectra showing the functional groups associated with these compounds formed in concrete exposed to internal chloride, and external chloride and composite chloride-sulfate solutions. In addition, the obtained FESEM images further substantiated the results obtained from XRD analysis. In case of exposure to chloride solutions, the variations in chloride binding capacity of concrete with cation type of chloride salts, and corrosion inhibitors are in line with the variations in the formations of calcium chloroaluminate (CCA) and chlorapatite as observed from the XRD analysis. The XRD and FESEM analyses confirmed the formation of more amount of calcium chloroaluminate (Friedel's salt) in the concrete admixed with corrosion inhibitors as compared to control mix. Besides, the XRD analysis indicated more formation of Friedel's salt in the concrete admixed with DHP than NaNO_2 . However, the formation of Friedel's salt decreased with increase in dosage of DHP whereas the opposite variation was observed in case of NaNO_2 . The XRD analysis also indicated the formation of calcium hypochlorite in the concrete subjected to MgCl_2 and CaCl_2 for both internal and external exposure conditions. However, the formation of calcium hypochlorite was more in case of MgCl_2 as compared to CaCl_2 . The XRD, FTIR spectroscopy, and FESEM analyses showed the formation of magnesium hydroxide in the concrete subjected to MgCl_2 solution, and formation of both magnesium hydroxide and gypsum in case of exposure to composite chloride-sulfate solutions. Further, the FESEM images indicated the formation of higher amount of C-S-H gel in PPC concrete as compared to OPC concrete. Besides, the microstructure of concrete examined through XRD, FTIR spectroscopy, and FESEM analyses indicated the formation of nitrite and phosphate based compounds in the concrete containing sodium nitrite, and di-Sodium hydrogen phosphate respectively.

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LIST OF SYMBOLS AND ABBREVIATIONS

θ	Diffraction angle of X-rays
λ	Wave length of X-ray
D_{app}	Apparent chloride diffusion coefficient
E_0	Half-cell potential (corrosion potential)
E_{eq}	Equilibrium potential
I_{corr}	Corrosion current density
R_p	Polarization resistance of steel reinforcement
t	Exposure time
x	Depth from exposure surface
x_c	Depth of convection zone
A	Chlorapatite /Hydroxyapatite
B	Brushite or dicalcium phosphate dehydrate
BT	Bearthite
BET	Brunauer-Emmett-Teller
C_F	Free chloride ion content
C_B	Bound chloride ion content
C_T	Total chloride ion content
C_s	Apparent surface chloride ion content
CC	Calcium chloride
CH	Calcium hydroxide or Portlandite
CP	Calcium phosphate
C_3A	Tricalcium aluminate
C_2S	Dicalcium silicate
C_3S	Tricalcium silicate
CCA	Calcium chloroaluminate or Friedel's salt
CCB	Calcium carbonate
CPES	Concrete powder electrolyte solution
C_4AF	Tetracalcium aluminoferrite
C-S-H	Calcium silicate hydrate
CaHPH	Acidic hydrated pyrophosphate
DHP	di-Sodium hydrogen phosphate
DOE	Department of Environment
E	Ettringite
EDX	Energy-dispersive X-ray
F	Feldspar
FTIR	Fourier Transform Infrared
FESEM	Field emission scanning electron microscope

G	Gypsum
HC	Calcium hypochlorite
IS	Indian standards
ICDD	International center for diffraction data
LPR	Linear polarization resistance
MC	Magnesium chloride
MH	Magnesium hydroxide or Brucite
MS	Magnesium sulfate
MSA	Maximum size of aggregate
M-S-H	Magnesium silicate hydrate
NC	Sodium chloride
OPC	Ordinary Portland cement
PDF	Powder diffraction file
PPC	Portland pozzolana cement
Q	Quartz
R	Chloride binding capacity
RIR	Reference-intensity ratio
SN	Sodium nitrite
SCE	Saturated calomel electrode
T	Thaumasite
TMT	Thermomechanically treated
XRF	X-ray fluorescence
XRD	X-ray diffraction
w/c	Water-to-cement

Introduction

1.1 General

Portland cement concrete is the most commonly used building material worldwide due to its excellent structural and durability properties, economic superiority, and minor requirements of maintenance [1-3]. Concrete is a composite material, which is generally made by mixing cementitious materials with aggregates, water, and chemical admixtures in suitable proportions [4, 5]. Steel reinforcement is used in concrete to provide higher tensile strength and/or ductility to the concrete structures [6]. In general, properly prepared, well maintained and compacted reinforced concrete possesses adequate durability properties and enhanced service life. However, many reinforced concrete structures exposed to aggressive environment have shown early deterioration and premature failure. This causes huge economic losses due to the repairing expenditure of deteriorated structures, which, in some cases, is almost equal to the construction cost of new structure [7]. Besides, the decrease in reliability and safety of the concrete structures also causes environmental, social, and industrial problems [7]. The durability of concrete depends on the service environment and exposure conditions, and is affected by corrosion of steel reinforcement (due to chloride ions and carbonation), sulfate attack, alkali-silica reaction, freezing/thawing cycles, etc. [2, 8]. Among these durability problems, corrosion of steel reinforcement is the most significant one that impacts the long-term performance of reinforced concrete structures during their service life. Generally, concrete provides both physical and chemical protection to the embedded steel bar [2, 9]. The physical protection of the steel bar is achieved by the impermeable concrete cover that retards the ingress of various agents such as oxygen, carbon dioxide, chloride ions, sulfate ions, and moisture to the level of steel bar. The chemical protection is achieved by the high alkalinity (pH value more than 12) of pore solution of concrete, which forms a microscopically thin, highly stable, and insoluble oxide film ($\gamma\text{-FeOOH}$ or $\gamma\text{-Fe}_2\text{O}_3$) on the surface of steel [2, 9, 10]. This oxide film (the passive film) minimizes the dissolution of iron that aids the steel reinforcement to remain in passive condition [11]. However, the passive layer is vulnerable as it can be destroyed by carbonation and/or attack by chloride ions thereby leading to the initiation of active steel reinforcement corrosion in concrete [9, 12]. Between carbonation and chloride attack, the steel reinforcement corrosion induced by chloride ions is more

detrimental due to its inhomogeneous distribution to a higher extent as compared to carbonation that leads to more unpredictable service life of reinforced concrete structures [13]. There are mainly two consequences of corrosion of steel reinforcement. First, the products of corrosion increase the volume by 3 to 4 times of original volume of steel bar, which results in cracking, spalling or delamination of concrete. Secondly, the cross-sectional area of the steel bar reduces, which results in reducing its load-carrying capacity and fatigue strength [14, 15].

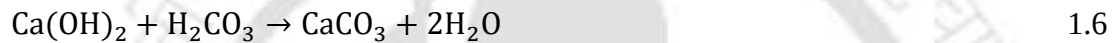
1.2 Reinforcement corrosion

Steel reinforcement corrosion is an electrochemical process that can be described as the flow of current from the anodic to cathodic site in the presence of oxygen and water [16-18]. Corrosion process gets initiated when there is a difference in electrical potential in the vicinity of steel reinforcement in concrete, which is responsible for set up of an electrochemical cell [15]. The electrochemical potentials are generated in two ways; firstly, when two different metals are embedded in concrete, or when the surface characteristics of embedded steel reinforcement have significant variations, composition cells may be formed [19]. Secondly, concentration cells may be formed in the vicinity of embedded steel reinforcement, which is attributed to the differences in the concentration of dissolved substances such as alkalis, oxygen, moisture, and chlorides [19]. As a result, in the steel reinforcement, one part becomes anode and the other part becomes cathode, which are connected by the electrolyte in the form of pore water present in the hardened cement paste [15, 19]. The positively charged ferrous ions Fe^{++} at the anode pass into the pore solution while the negatively charged free electrons e^- travel from anode to the cathode through the steel where they are absorbed by the constituents of the electrolyte and combine with water and oxygen to form hydroxyl ions $(\text{OH})^-$ [15, 18]. The hydroxyl ions $(\text{OH})^-$ travel from cathode to anode through the concrete pore solution and combine with the ferrous ions to form ferrous hydroxide which, on further oxidation gets converted to rust [15, 18]. The electrochemical reactions involved are as follows [15]:



1.2.1 Carbonation induced steel reinforcement corrosion

Carbonation is a physicochemical reaction between carbon dioxide and hydrated cement. In carbonation, carbon dioxide penetrates into the concrete from atmosphere and forms carbonic acid in the presence of moisture [4, 20]. The carbonic acid further reacts with calcium hydroxide (liberated from hydration reaction) to form calcium carbonate thereby neutralizing the alkalinity of concrete pore solution. Thus, the pH of concrete pore solution decreases to a value lower than 9 [4, 20]. At this low pH value, the passive film is not thermodynamically stable and gets destroyed thereby leaving the steel bar unprotected to the effect of corrosion in concrete [21]. The chemical reactions of carbonation process in concrete are as follows [4, 20]:



1.2.2 Chloride induced steel reinforcement corrosion

Chloride ions cause macrocell corrosion also known as non-uniform or localized corrosion of steel reinforcement, where the anodic site (i.e. the active part of steel) and cathodic site (i.e., the passive part of steel) are distant from each other [22]. Chloride ions can enter into the fresh concrete along with mix ingredients (such as chloride contaminated aggregates, chloride contaminated mixing water, and chloride bearing admixtures) at the time of preparation and/or can enter into the hardened concrete by the use of deicing salts, and from seawater and ground water [23, 24]. In concrete, chloride ions exist in two forms: as free chloride in concrete pore solution, and in bound form, where the chloride ions are physically adsorbed or chemically bound with the hydration products of cementitious materials through complex reactions. Chloride ions are physically adsorbed on the calcium silicate hydrate (C-S-H), which alters the C-S-H to a cellular and porous structure that leads to the disruption of the hardened concrete [25]. The interaction between chloride ions and C-S-H gel occurs in three different ways: (i) chloride ions may be present in a chemisorbed layer on the hydrated calcium silicates, (ii) it may penetrate into the spaces available in C-S-H interlayer, or (iii) it may be intimately bound in the C-S-H lattice [23]. In addition, chloride ions chemically react with the cementitious materials, and form Friedel's salt ($\text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$) and Kuzel's salt ($\text{C}_3\text{A} \cdot 0.5\text{CaCl}_2 \cdot 0.5\text{CaSO}_4 \cdot 10\text{H}_2\text{O}$) [25-28]. Generally, it is considered that free chloride plays a major role in the process of steel reinforcement corrosion [29]. On the other hand, the bound chloride plays an important role in the chloride

transport process in concrete [30]. For the same content of total chloride, the formation of more amount of bound chloride reduces the amount of free chloride [31].

The risk of corrosion of steel reinforcement in concrete increases as the ratio of the concentration of chloride ions to that of the inhibitive hydroxyl ion in the pore solution increases [12]. To destroy the passive layer of steel and initiate the chloride induced corrosion, the chloride ion content at the rebar level should be above the threshold limit. The reactions involved in the presence of chloride ions are as follows [15]:



The other reactions, and especially the cathodic reaction, are same as that in the absence of chloride ions in concrete.

1.3 Chloride diffusion in concrete

Chloride ions enter into the concrete through several transportation mechanisms, namely diffusion, migration, capillary sorption (or convection), and permeation [32-34]. Among them, diffusion process is considered as the governing mechanism for ingress of chloride ions into the saturated concrete [32-36]. Diffusion of chloride ions is a complex physicochemical process that includes ionic actions and multiphase reactions [37]. In concrete, the diffusion of chloride ions is affected by many factors, which are partly related to the concrete characteristics, and partly to the composition of exposure solution [38]. Thus, the presence of other ions along with chloride ions in the exposure solution or in the concrete pore solution may greatly influence the diffusion behaviour of chloride ions in concrete. Various analytical models obtained from theories, and empirical models based on experimental results have been used by the researchers to analyze the chloride ion distribution in concrete [39]. However, Fick's second law of diffusion is widely used to describe the chloride ion transport in concrete considering one-dimensional flow of chloride ions in a semi-infinite medium [40] and is as follows [39]:

$$\frac{\partial C}{\partial t} = D_{app} \frac{\partial^2 C}{\partial x^2} \quad 1.9$$

Where, $C = C_{(x,t)}$ denotes the chloride ion content (%) as a function of x (depth from exposure surface) and t (exposure period), and D_{app} is the apparent chloride diffusion coefficient of concrete.

An error function solution to the Fick's second law of diffusion can be written as [41],

$$C_{(x,t)} = C_s \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{D_{app}t}} \right) \right] \quad 1.10$$

Where, C_s represents the apparent surface chloride ion content (%), and erf is the Gauss error function: $\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$.

The chloride diffusion coefficient is an important parameter in the estimation of service life of reinforced concrete structures affected by chloride-induced steel reinforcement corrosion [42].

1.4 Chloride binding capacity of concrete

Chloride binding is one of the most important factors for ingress of chloride ions and steel reinforcement corrosion in concrete structures exposed to chloride environment [43]. As stated earlier, chloride binding is the process where the chloride ions are captured by the hydration products of concrete through two different mechanisms of ionic binding i.e., physical process and chemical process [44, 45]. Chloride binding is a significant parameter while studying the service life of reinforced concrete structures, for the following reasons [44, 46]:

- Chloride binding reduces the free chloride content in the vicinity of the steel reinforcement, which reduces the chance of steel reinforcement corrosion,
- Chloride binding removes the chloride ions from the diffusion flux thereby retarding the penetration of chloride to the surface level of steel reinforcement,
- Formation of Friedel's salt (formed due to reaction between chloride ions, and aluminiferous and ferruginous compounds) results in a denser pore structure in concrete due to filling of pores that slows down the transport of chloride ions.

The binding of chloride ions in concrete is influenced by many factors such as content of reactive alumina phase present in cement, alkalinity of concrete pore solution, type of supplementary cementitious materials, cation type associated with chloride ions, curing condition, carbonation, chloride ion concentration, sulfate ions, temperature, w/c, and microstructure of concrete etc. [23, 46-48].

The relationship between change of total chloride content and that of free chloride content is defined as the chloride binding capacity of concrete [49]. As the total chloride content in concrete is the sum of free and bound chloride ions, the chloride binding capacity of

concrete can be defined in terms of bound chloride and free chloride contents as shown in Eq. 1.11 [49, 50].

$$R = \frac{\partial C_B}{\partial C_F} \quad 1.11$$

Where R = chloride binding capacity, C_F = free chloride ions content, C_B = bound chloride ions content.

1.5 Effect of cation type associated with chloride ions on chloride ingress

Although chloride ions are mainly responsible for corrosion of steel reinforcement but they never exist in isolation in the exposure environment [51]. Chloride ions co-exist with different cations in the service environment of reinforced concrete structures in the form of chloride salts [37]. The common types of cation that are associated with the chloride ions in different exposure environment such as marine environment, deicing salts, salt lakes, and contaminated soil and groundwater etc. are Na^+ , Ca^{2+} , Mg^{2+} , and K^+ [37, 52]. The cations associated with chloride ions also play a major role in the process of chloride diffusion, chloride binding and eventually on the chloride induced steel reinforcement corrosion in cement composites [37, 51-56]. The cations mostly diffuse into the concrete at a slower rate as compared to anions due to their lower drift velocity than anions [36, 38, 51]. Once anions move forward, a counter-electrical field will be formed between the anions and the surrounding cations [36]. The combination of driving force of anions (due to chemical potential gradient) and draw-back force of cations (counter-electrical field) is known as electrochemical potential [36]. As the diffusion of anions must be accompanied by the cations, the lower drift velocity of cations retards the diffusion rate of anions [36, 51]. Previous literature have reported that that the chloride ions associated with divalent cations have higher diffusion coefficient as compared to the chloride ions associated with monovalent cations [54, 57]. However, another study reported that the trend of diffusion coefficient of chloride ions with the associated cations in concrete depends on the test method (i.e., steady method or unsteady method) [37]. Cation associated with a smaller number of anions is likely to have less chloride binding capacity as compared to the cation associated with more number of anions [51]. In addition, different cations associated with chloride ions are responsible for changes in the microstructure of concrete [26, 52]. The presence of higher concentrations of cations (e.g., Ca^{2+} and Mg^{2+}) associated with chloride ions can react with hydrated cement products and form complex salts such as calcium oxychloride and magnesium oxychloride respectively, which may cause severe cracking and chemical degradation of hardened concrete [26, 58].

1.6 Sulfate attack

Sulfate attack is another severe problem that affects the durability and service life of concrete structures. Sulfate attack is of two types such as physical sulfate attack (due to salt crystallization) and chemical sulfate attack [59]. Physical sulfate attack causes surface deterioration and surface scaling of the above ground portion of concrete that is partially immersed in sulfate rich soil [59, 60]. Chemical sulfate attack is caused by the chemical reactions between sulfate ions and the cement hydration products that results in the formation of expansive products namely secondary ettringite (AFt), gypsum and brucite (magnesium hydroxide) in concrete [47, 59-64]. Gypsum and ettringite occupy a larger volume that causes expansion and cracking of concrete eventually leading to the degradation of stiffness and strength of concrete [46, 65-67]. Sulfate ions enter into the hardened concrete by diffusion process or capillary suction from sulfate rich soil, ground water or marine environment, which contain sulfate salts in the form of calcium sulfate, sodium sulfate, potassium sulfate and magnesium sulfate [15, 46, 67]. In sulfate environment, concrete structures situated in water table fluctuation zone, tidal zone, and splash zone are more vulnerable to sulfate attack because of drying-wetting cycles, which can accelerate the diffusion process of sulfate ions [67, 68].

1.7 Corrosion inhibitors

Many new materials and technologies have been developed with an objective to increase the service life of reinforced concrete structures against corrosion of steel reinforcement [69]. These methods include variation of the concrete formulation, addition of mineral admixtures, chloride extraction, cathodic protection, application of protective coatings and sealers, concrete re-alkalization, and use of corrosion inhibitors, which can be adopted to prevent and mitigate the corrosion of steel reinforcement in concrete [2, 69-78]. Among the available methods, use of corrosion inhibitors is one of the most convenient, attractive and cost-effective method to prevent or control corrosion of steel reinforcement in concrete [70, 80-84]. By definition, corrosion inhibitor is a chemical compound, either in liquid or powder form, which when introduced into the concrete in suitable amount can effectively prevent or slow down the corrosion of steel reinforcement embedded in concrete and has no adverse effect on the fresh and hardened properties of concrete [1, 85]. The main advantage of corrosion inhibitors against corrosion of steel reinforcement is that they are uniformly distributed all over the concrete matrix and protect the entire surface of steel reinforcement [1].

1.7.1 Types of corrosion inhibitors

Depending on the mode of application, inhibitors can be classified as preventive and curative corrosion inhibitors [86]. The preventive corrosion inhibitors are introduced to the fresh concrete during the preparation of concrete with the mixing water [86]. These inhibitors are applied in reinforced concrete to strengthen the passive film over the steel reinforcement [86]. In concrete where the contamination of chloride ions and/or carbonation is already initiated, the preventive corrosion inhibitors delay the onset of corrosion process and thereby minimize the rate of initiated steel reinforcement corrosion [86]. The curative corrosion inhibitors are also known as penetrating or migrating corrosion inhibitors. These inhibitors are directly applied on the exploited and corroded surface of hardened reinforced concrete structures [86]. They penetrate through the concrete cover and reach the steel to suppress the ongoing corrosion of steel reinforcement [86]. Corrosion inhibitors can also be classified in three categories according to their protection mechanisms as anodic or active corrosion inhibitors, cathodic or passive corrosion inhibitors, and mixed or passive-active corrosion inhibitors [5, 18, 79, 85].

1.7.2 Anodic corrosion inhibitors

Anodic corrosion inhibitors function due to their ability to accept electrons. They act on the dissolution of steel reinforcement and reduce the corrosion rate by an increase in the corrosion potential value of the steel [18]. At the anode, these inhibitors actively interfere with the corrosion process, and suppress the anodic reaction by oxidizing the ferrous ions to insoluble ferric oxide [5, 85]. This results in stabilization of the passive film over the steel, which reduces the rate of corrosion reaction [87]. Anodic corrosion inhibitors include various organic and inorganic compounds such as sodium benzoate, calcium nitrite, sodium nitrite, sodium chromate, potassium chromate, stannous chloride, sodium silicate and sodium phosphate [85]. Among them, nitrite-based compounds such as calcium nitrite and sodium nitrite were widely studied and used as corrosion inhibitors to minimize steel reinforcement corrosion in the presence of chloride ions [6, 88-91].

1.7.3 Cathodic corrosion inhibitors

Cathodic corrosion inhibitors indirectly interfere with the corrosion process by slowing down the cathodic corrosion reaction [5, 85]. They form an insoluble film on the cathodic surface of the steel and restrict diffusion of reducible species, such as oxygen [85, 92]. The bond between the reactive product of cathodic inhibitors and the metal is not strong, and

hence the effectiveness of cathodic corrosion inhibitors may be less as compared to anodic corrosion inhibitors [85]. The compounds used as cathodic inhibitors include aminoethanol group, sodium hydroxide, ammonium hydroxide, sodium carbonate, and calcium carbonate, etc. [5, 85].

1.7.4 Mixed corrosion inhibitors

Mixed corrosion inhibitors influence both the anodic and cathodic regions by forming salts as they accept either the available electrons or protons [5, 18, 92]. They are generally adsorbed over the steel surface and form a thin protective layer thereby minimizing the corrosion rate of steel reinforcement without a significant variation in the corrosion potential of steel [18, 92]. Mixed corrosion inhibitors are typically organic compounds such as amines, alkanolamines, fatty acids, etc. [92, 93]. The mixed corrosion inhibitors may also be a physical combination of two compounds in which, one part of the mixture participates in the cathodic reaction site while the other part participates at the anodic reaction site of corrosion reaction [5].

1.7.5 Basic mechanism of protection of corrosion inhibitors

Each of the corrosion inhibitor groups may include materials that mitigate corrosion by different inhibition mechanisms, which include: formation of protective film over steel surface through competitive surface adsorption process between chloride ions and corrosion inhibitor; by increasing or buffering of pH in the local (pit) environment; and by competitive migration of chloride ions and inhibitor into the pit [14, 18, 94]. In addition to corrosion inhibiting mechanism, some corrosion inhibitors also block the pores in concrete thereby delaying, or minimizing the diffusion of chloride ions [25, 95, 96]. The pore blocking behavior is a secondary property of some corrosion inhibitors [18, 97].

The effect of different corrosion inhibitors on corrosion potential and corrosion current density are shown in Fig. 1.1 [98]. The figure depicts the anodic and cathodic half-cell reaction rates (i.e., corrosion currents) as a function of the corrosion potential at the interface of steel/concrete. In absence of any corrosion inhibitor, the anodic and the cathodic corrosion reactions are represented by the solid lines and the corresponding equilibrium values of corrosion potential and corrosion current density are represented by E_1 , and i_1 respectively. In the presence of an anodic corrosion inhibitor, the corrosion potential will be raised to a level E_2 , and the corresponding corrosion current density will be decreased to i_2 . At this point, the anodic and cathodic curves intersect each other in the

passive region of the anodic curve as indicated in the figure (Fig. 1.1), by the dashed line named as “anodic inhibitor”. In the presence of a cathodic inhibitor, the cathodic reaction rate will be reduced. At this point, both the corrosion potential and corrosion current density will decrease to E_3 , and i_3 respectively as shown by the dashed line named as “cathodic inhibitor”. The use of a corrosion inhibitor that blocks the concrete pores will limit the oxygen ingress, and thus, reduce the cathodic current thereby giving values of corrosion potential and corrosion current density as E_4 , and i_4 respectively as indicated by the dashed line “pore blocker” in Fig. 1.1 [98].

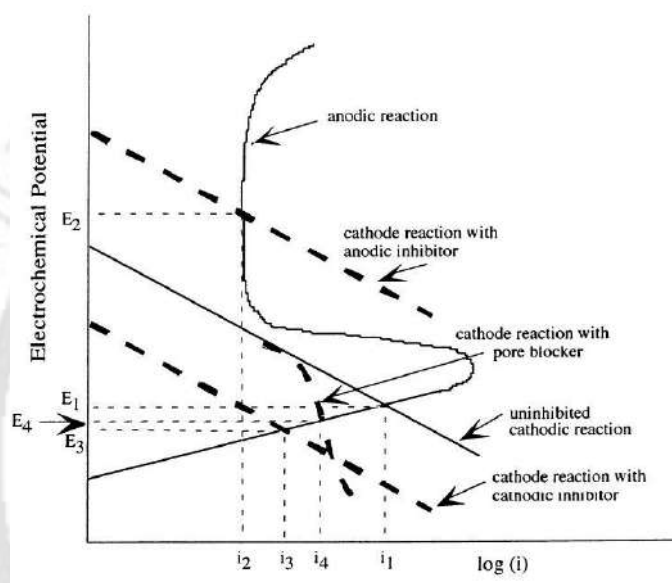
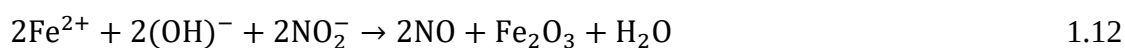


Fig. 1.1 Effect of inhibitors on corrosion potential and corrosion current density [98]

1.7.6 Nitrite based corrosion inhibitors

Nitrite based corrosion inhibitors have oxidizing properties and they act as a passivator [90]. They oxidize the ferrous ions, the first product of corrosion into insoluble and stable ferric oxide, which adheres tightly to the surface of steel reinforcement. The governing reactions are as follows [3, 18, 85, 88, 89, 99, 100]:



As compared to other nitrite based corrosion inhibitors, calcium nitrite is the most preferred and used corrosion inhibitor due to its compatibility with the properties of concrete [92]. Calcium nitrite increases the chloride threshold level and corrosion-free service life of reinforced concrete structure, which signifies that it has prominent inhibiting effect against

corrosion of steel [11, 92]. Sodium nitrite enhances the corrosion resistance properties of concrete exposed to sodium chloride solution [80, 84]. The effectiveness of nitrite based corrosion inhibitors depends on nitrite to chloride molar ratio [90]. To maintain passivity and prevent corrosion of steel reinforcement, the nitrite to chloride molar ratio should be more than 0.8 - 1 [90]. Some of the limitations with the use of nitrite based corrosion inhibitors include possible toxic effects, solubility, mechanical losses of concrete, and possible increase in corrosion rate, if not added in sufficient quantities or if used in concrete with cracks [12, 90].

1.7.7 Phosphate based corrosion inhibitors

Phosphate based compounds were studied as alternative corrosion inhibitors because phosphates have some advantages such as low cost and low toxicity [96, 101, 102]. Phosphate ions get adsorbed onto the passive iron oxide film, and delay the initiation of corrosion of steel by displacing the chloride ions from the steel surface [101, 102]. There is no clarity about the efficiency and inhibition mechanism of phosphate based inhibitors [101, 102]. According to previous studies, phosphate ions have a dual effect. Firstly, calcium phosphate, the product of phosphate and calcium hydroxide reaction, blocks the pores of concrete and reduce the diffusion of aggressive ions into the concrete. Secondly, iron phosphate, the product of the reaction between iron and phosphate ions, could block the cathodic or anodic sites [101]. Previous studies indicate that use of phosphate based inhibitors can change the mechanical properties of concrete or modify the curing time due to the precipitation of calcium phosphate [101]. Some researchers have suggested phosphates as non-oxidizing anodic inhibitors, which are only effective against corrosion in the presence of oxygen [102-104]. On the other hand, some other researchers have concluded that if $[\text{PO}_4^{-3}]/[\text{Cl}^-]$ ratio is less than 0.6, phosphates act as cathodic corrosion inhibitors and when $[\text{PO}_4^{-3}]/[\text{Cl}^-]$ ratio is more than 0.6, they act as mixed corrosion inhibitors [18, 105].

1.8 Organization of the thesis

The research work carried out in the present investigation has been organized in eight chapters as mentioned below.

- **Chapter 1**

In this chapter, the research area is briefly introduced with an overview of the durability problems encountered in concrete, chloride diffusion, chloride binding,

and use of corrosion inhibitors. Further, Chapter 1 also includes the organization of the thesis.

▪ **Chapter 2**

In this chapter, the review of literature related to the present research work is described. The literature review related to the effects of cement type, w/c, cation type of chloride salts, and exposure environment on corrosion of steel reinforcement in simulated concrete pore solution as well as in cementitious composites in the presence of different corrosion inhibitors are presented. In addition, the review of literature related to the effect of above parameters on chloride diffusion and chloride binding in cementitious composites are also presented in this chapter. Further, the reported research works on microstructure of concrete subjected to different exposure environment are also presented. From the review of literature, the research gap related to the present research work is identified. Based on the research gap in the literature, the objectives of the present research work have been formulated and are presented in Chapter 2.

▪ **Chapter 3**

This chapter presents the details of the experimental work carried out to fulfill the objectives of the present research work. The details about the materials, mix proportion, preparation of test specimens, exposure solutions and various tests carried out on the test specimens are presented in this chapter.

▪ **Chapter 4**

In this chapter, the results obtained from the experimental investigation on the effect of different chloride salts on corrosion behaviour of steel reinforcement by carrying out potentiodynamic polarization test in concrete powder electrolytic solution (CPES) in the presence of corrosion inhibitors are presented and discussed. Compressive strength of concrete was determined to evaluate the effect of chloride ions and corrosion inhibitors on the mechanical property of concrete and the obtained results are presented and discussed in this chapter. Further, the effect of cation type of chloride salts on chloride binding in concrete was analyzed and discussed. In addition, to examine the microstructure of concrete in the presence of chloride ions and corrosion inhibitors, the obtained results of X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy analyses are analyzed and discussed in this chapter.

▪ **Chapter 5**

In this chapter, the obtained results of half-cell potential, and corrosion current density (by linear polarization resistance (LPR) measurement) of steel reinforcement in cylindrical reinforced concrete specimens admixed with corrosion inhibitors and different chloride salts are presented. The variations in half-cell potential and corrosion current density of steel reinforcement with cement type, cation type of admixed chloride salts, corrosion inhibitors, and exposure duration are analyzed and discussed in this chapter. Further, the obtained results of XRD, FTIR, and Field emission scanning electron microscope (FESEM) analyses on concrete powder samples collected from the rebar level (i.e., 25-30 mm) of cylindrical reinforced concrete specimens are analyzed and discussed in Chapter 5.

▪ **Chapter 6**

This chapter presents and discusses the results obtained from half-cell potential and corrosion current density by LPR measurement on steel reinforcement in cylindrical reinforced concrete specimens exposed to chloride and composite chloride-sulfate solutions. The variations in half-cell potential and corrosion current density of steel reinforcement with cement type, w/c, exposure solution i.e., chloride solution and composite chloride-sulfate solution, cation type of chloride salts, corrosion inhibitors, and exposure duration are examined and discussed in this chapter. Further, the obtained results of microstructure analysis (i.e., XRD, FTIR and FESEM analyses) are presented in this chapter to study the changes in microstructure of concrete exposed to chloride and composite chloride-sulfate solutions.

▪ **Chapter 7**

In this chapter, the obtained results of free chloride profile of concrete powder samples collected at the end of exposure period from varying depth intervals of cube specimens exposed to chloride and composite chloride-sulfate solutions are presented. Further, the effects of cement type, w/c, exposure solutions (i.e., chloride solution and composite chloride-sulfate solution), cation type of chloride salts, and corrosion inhibitors on variations in free chloride content, apparent chloride diffusion coefficient and chloride binding capacity of concrete are analyzed and discussed in Chapter 7. In addition, the effects of above parameters on microstructure of concrete (through XRD, FTIR and FESEM analyses) are also discussed in this chapter.

▪ **Chapter 8**

In this chapter, all the conclusions drawn from the present research work are presented. Besides, the recommendations for future research work are also presented in this chapter.



Literature Review

2.1 General

In this chapter, the research work carried out by various researchers to evaluate the effect of different types of corrosion inhibitors against steel reinforcement corrosion in simulated concrete pore solution as well as in cementitious composites for exposure to different aggressive environment especially chloride exposure are presented. Further, the reported research work on the effect of different corrosion inhibitors on chloride ingress, and chloride binding in cementitious composites are presented, wherein the effect of different parameters such as binder type, w/b, and exposure condition (exposure solutions, wetting-drying cycle, exposure duration, etc.) on the above mentioned parameters are discussed. In addition, the research work on the effect of cation type associated with chloride ions on steel reinforcement corrosion, chloride ingress, and chloride binding of cementitious composites exposed to chloride and composite chloride-sulfate solutions are discussed. Further, the research works carried out by various researchers on the effect of binder type, w/b, corrosion inhibitors, cation type of chloride salts, and exposure condition on variations in microstructure of cementitious composites are presented. Subsequently, the summary of literature review, and research gap in the literature followed by the objectives of the present research work are presented in this chapter.

2.2 Effect of corrosion inhibitors against steel reinforcement corrosion in simulated concrete pore solution

The reported research work in the literature on inhibition effect of different corrosion inhibitors against corrosion of steel reinforcement in simulated concrete pore solutions in the presence of chloride ions are presented in this section. Further, the effects of cement type, chloride concentration, presence of sulfate ions, and pH of simulated pore solution on the performance of corrosion inhibitors are discussed. In addition, the reported research work on the effect of corrosion inhibitors on the microstructure of steel surface exposed to simulated pore solutions are also discussed in this section.

Joseph and Perret [106] have experimentally investigated the effect of corrosion inhibitor on corrosion of steel in salt-water solution using chemical corrosion tests, direct immersion test, and galvanostatic anodic-polarization measurement. For this purpose, mild steel bars

of 15.6 mm diameter, and 13.5 to 18 mm length were used as test specimens. The test solutions were prepared by mixing distilled water with sodium chloride (NaCl, as a source of chloride ions) and sodium nitrite (NaNO₂, as corrosion inhibitor). In this study, three concentrations (i.e., 0.5%, 0.8% and 1%) of sodium chloride and one concentration (i.e., 2%) of sodium nitrite for chemical corrosion test, and 26 concentrations each of sodium chloride (i.e., from 0.1% to 1%), and sodium nitrite (i.e., from 0.025% to 1.2%) were used for direct immersion test. For galvanostatic anodic-polarization measurement, sodium chloride at the concentrations of 0.5%, 0.8% and 1%; and sodium nitrite at the concentrations of 0.5%, 0.6% and 1% were used. Besides, pH of test solutions used for galvanostatic anodic-polarization measurement was also measured. Based on the obtained results, the authors concluded that complete inhibition against corrosion was obtained only when NaNO₂ : NaCl ratio was equal to or higher than 0.8. The break-through potential increased from 40 mV to 120 mV as the NaNO₂ : NaCl ratio was increased from 0.75 to 2.0. At low current densities, the pH values were fairly stable in the range of 6.2 to 6.9, whereas at higher current densities where pitting was observed, the pH reached a value of 9.6.

Monticelli et al. [107] have studied the use of di-sodium β -glycerophosphate (GPH) as a nontoxic corrosion inhibitor against reinforcement corrosion in alkaline chloride solution and compared with sodium nitrite. Saturated Ca(OH)₂ solution admixed with 0.1 M chloride (calcium chloride), which simulates the characteristics of electrolyte present in concrete pores was used as the test solution. Corrosion inhibitors namely di-sodium β -glycerophosphate (0.05 M), sodium nitrite (0.05 M), and mixtures of 0.005 M GPH (di-sodium β -glycerophosphate) and 0.005 M sodium nitrite were added to the test solutions. In this study, potentiodynamic polarization measurement, electrochemical impedance spectroscopy, electrochemical noise analysis and electron probe microanalysis were carried out on steel samples (having geometric area of approximately 4.5 cm²) exposed to alkaline chloride solutions for 20 days. From the obtained results, the authors reported that di-sodium β -glycerophosphate (GPH) exhibited good inhibiting efficiency towards the localized attack, which was almost comparable to that exhibited by sodium nitrite. The mixtures of 0.005 M GPH and 0.005 M sodium nitrite also showed good inhibiting action against the localized attack although low concentration of both inhibitors was used. The calcium ions play a twofold role in the inhibition mechanism of GPH: by facilitating the

transport of the phosphonate ion and its adsorption on the steel surface, and by incorporation in the surface passive film of steel.

Etteyeb et al. [108] have carried out an experimental investigation to evaluate the inhibiting efficiency of sodium phosphate (Na_3PO_4) against corrosion of carbon steel in alkaline medium simulating the interstitial solution of concrete (pH 12.5) contaminated with chloride ions. The authors have applied the corrosion inhibitor in two ways: in the first method, Na_3PO_4 (0.5 M) was added to the simulated concrete pore solution admixed with 0.5 M NaCl, and in the second method, the rebar was first pre-treated by submerging it in 0.5 M Na_3PO_4 solution and then immersed in chloride contaminated (0.5 M NaCl) pore solution. The authors performed electrochemical impedance spectroscopy (EIS), electrochemical quartz crystal microbalance (EQCM), and polarization measurements at 2 and 72 hours of exposure period. The results showed that the pretreatment of steel with Na_3PO_4 provides good protection against corrosion by the formation of a protective layer on the surface of steel that prevents the ingress of aggressive anions to the steel interface. The results also indicated that the pretreatment of steel by Na_3PO_4 provides inhibiting efficiency of more than 99% whereas, in case of inhibitor added to the pore solution, the inhibiting efficiency was less than 90%. Gravimetric measurements obtained by electrochemical quartz crystal microbalance (EQCM) showed that the mass of the products formed at the steel interface increases with time indicating increase in the thickness of the passive film formed on the surface of steel.

Etteyeb et al. [109] have carried out an experimental study to evaluate the inhibiting efficiency of three phosphate based compounds against corrosion of steel reinforcement in alkaline solutions using open circuit potential measurement, linear polarization resistance (LPR) measurement, electrochemical impedance spectroscopy, polarization curves, and gravimetric loss measurement. The authors have prepared the test solutions using saturated $\text{Ca}(\text{OH})_2$ solution admixed with 3% NaCl. Three types of phosphate based inhibitors such as sodium phosphate (Na_3PO_4 : SP, at the dosage of 3%), tetrasodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$: TSPP, at the dosage of 3%), and hydroxyethylidene-diphosphonic acid ($\text{C}_2\text{H}_8\text{O}_7\text{P}_2$: HEDP, at the dosage of $10^{-2}\%$) were added in the test solutions. Steel specimens of 6 mm diameter and exposed area of 5.65 cm^2 were used as the test specimens and immersed in saturated $\text{Ca}(\text{OH})_2$ solution admixed with and without chlorides during the testing period of 30 days. The obtained results showed that in alkaline solution without chloride, phosphate based compounds formed a protective layer over the steel surface. In

the presence of chloride ions, sodium phosphate (SP) acts as an anodic inhibitor and increases the pitting potential and decreases the corrosion current density of steel, which shows the protecting effects of this compound. The steel exposed to TSPP and HEDP showed higher corrosion current density (from LPR measurement) and corrosion rate (from gravimetric measurement) as compared to that exposed to sodium phosphate (SP). The authors reported that the HEDP loses its inhibition efficiency probably due to the decrease of pH and/or may be due to high $[\text{Cl}^-]/[\text{inhibitor}]$ ratio.

Tommaselli et al. [3] have carried out an experimental study to evaluate the effect of sodium nitrite and sodium molybdate as corrosion inhibitors in saturated calcium hydroxide solution contaminated with sulfuric acid and nitric acid. Carbon steel bar of 2.5 mm diameter and 60 mm length was used as the steel reinforcement. In the study, saturated $\text{Ca}(\text{OH})_2$ solution (pH 12.5) was prepared by adding $\text{Ca}(\text{OH})_2$ at the concentration of 1.2 g/l in distilled water. To acidify and lower the pH (pH 8) of $\text{Ca}(\text{OH})_2$ solution, sulfuric acid and nitric acid were added in the molar ratio of 2:1 to the test solution. The corrosion inhibitors i.e., sodium nitrite and sodium molybdate were added in the acidified $\text{Ca}(\text{OH})_2$ solution at the dosages of 0%, 11%, 16%, 22%, 33% and 38% by mass of calcium hydroxide for anodic polarization measurement, while for AC impedance measurements the inhibitors were added in the acidified $\text{Ca}(\text{OH})_2$ solution at the dosages of 0%, 11%, 22%, and 33% by mass of calcium hydroxide. From the obtained results, the authors have observed that at low dosages, sodium molybdate showed higher inhibiting effect (efficiency of about 67%) as compared to sodium nitrite (efficiency of about 52%). However, at higher dosages, both the corrosion inhibitors displayed similar, and higher inhibiting effect i.e., efficiency of about 80%.

Mennucci et al. [110] have investigated the effect of benzotriazole (BTAH) on the corrosion of carbon steel in simulated chloride-contaminated concrete pore solution. The simulated chloride-contaminated pore solution was composed of 2.8 weight % of KOH, 0.4 weight % of NaOH, and 3.5 weight % of NaCl. Benzotriazole was added to the simulated chloride-contaminated pore solution at the concentration of 1.5 weight %. In addition, a reference solution was also prepared by adding 1.5 weight % of nitrite to the simulated chloride-contaminated pore solution for comparison of the effect of nitrite and (BTAH) on corrosion resistance of steel reinforcement. Corrosion of steel was investigated by carrying out immersion test, and electrochemical tests namely electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurement on carbon steel

specimens having exposed areas of 1 cm^2 , and 0.875 cm^2 respectively for immersion test, and electrochemical tests. In case of immersion test, steel samples were immersed in BTAH solution for a period up to 30 days, and the exposed areas of steel were examined by optical microscopy (OM) and scanning electron microscope (SEM) at 1, 6, 15, and 30 days of exposure. Further, Raman microscopy, and infrared (IR) studies for surface film characterization of steel were also performed after steel specimens were exposed to the simulated chloride-contaminated pore solution for 6 months, and 90 days respectively. Based on the obtained results, the authors have concluded that the addition of BTAH significantly increased the corrosion resistance of steel and the improvement in the corrosion resistance of steel due to BTAH was superior to that associated with nitrite for similar inhibitor concentration. The increased inhibition efficiency of BTAH was attributed to the formation of a complex layer of $[\text{Fe}_n(\text{Cl})_p(\text{BTA})_m]$ that covers the steel surface, and acts as a partial barrier against the ingress of aggressive species. The authors suggested that BTAH is a potentially attractive alternative to nitrites for inhibiting corrosion of steel reinforcement in concrete.

Song et al. [111] have carried out an experimental investigation to evaluate the influence of alkaline nitrites such as NaNO_2 , KNO_2 , and $\text{Ca}(\text{NO}_2)_2$ on inhibition of corrosion of steel in binary and ternary cement systems. The authors have used three types of cement namely ordinary Portland cement (OPC), Portland pozzolana cement (PPC), and Portland slag cement (PSC) to prepare cement extracts. The binary systems used in the research work include (OPC + PSC), (OPC + PPC), (PPC + PSC) and a ternary system was used by mixing OPC, PPC, and PSC. The steel specimens of size 12 mm diameter and 60 mm length were exposed to different cement extract solutions, and cement extract solutions containing NaCl (1%, 2%, and 3%) and different nitrites (0.5%) for a period of 6 months followed by weight loss measurement of steel. The authors have also performed electrochemical measurements such as open circuit potential measurements, potentiodynamic polarization measurement, and A.C. impedance measurement on steel in binary and ternary cement extract solutions, and cement extract solutions containing different percentages of NaCl (1%, 2%, and 3%) and 0.5% NaNO_2 . The potentiodynamic polarization measurement was performed on the steel specimen of exposed area 1 cm^2 in the cement extracts. In addition, pH values of both binary and ternary cement extracts were also measured. From the results of weight loss measurement, the authors have observed that the efficiency of different nitrites in reducing the corrosion of steel in binary and ternary cement systems was in the order: $\text{NaNO}_2 >$

$\text{KNO}_2 > \text{Ca}(\text{NO}_2)_2$. Further, the results obtained from electrochemical measurements showed that among the binary cement system, NaNO_2 was more effective in decreasing the corrosion in OPC + PSC system. The composite cement provided better protection for steel in concrete, especially the ternary system, which showed an inhibiting efficiency of 91% in the presence of 1% chloride and 0.5% nitrite. Further, the use of binary and ternary cement systems did not influence the pH of cement extracts.

Garces et al. [112] have studied the influence of pH on the inhibition effect of sodium nitrite (NaNO_2) against corrosion of reinforcing steel in simulated concrete pore solution contaminated with chlorides. For this purpose, simulated concrete pore solutions of different pH (pH 7 to pH 11) were prepared by adding different volumes of FeCl_2 (0.2 M) to saturated calcium hydroxide solution. Four sets of test solutions were prepared with or without sodium nitrite such as: (a) without NaNO_2 , (b) with 0.1 M NaNO_2 , (c) with 0.5 M NaNO_2 , and (d) without NaNO_2 for 28 days, then the addition of 0.1 M NaNO_2 for 9 days followed by addition of more NaNO_2 till the concentration reached 0.5 M. The extent of corrosion of steel bars with exposed area of 12.04 cm^2 and exposed to simulated concrete pore solutions were measured by polarization resistance measurement and electrochemical impedance spectroscopy technique. The conductivity and pH of the simulated concrete pore solution were also measured during and at the end of electrochemical tests. In addition, gravimetric mass loss test was also carried out on the steel specimens exposed to different simulated concrete pore solutions. Based on the obtained results, the authors reported that the addition of 0.1 M NaNO_2 significantly decreased the corrosion rate and shifted the corrosion potentials of steel towards more noble values as compared to the solution without NaNO_2 for simulated concrete pore solutions with pH ranging from 7 to 11. The addition of 0.5 M NaNO_2 decreased the corrosion rate of steel in simulated concrete pore solutions with pH ranging from 9 to 11. Further, with decrease in pH of simulated concrete pore solutions, the efficiency of NaNO_2 decreased, and in solution with pH 7, 0.5 M NaNO_2 showed corrosion rate even worse than the solution without NaNO_2 .

Shi and Sun [80] have experimentally studied the inhibiting efficiencies of three corrosion inhibitors in preventing chloride induced steel reinforcement corrosion in simulated concrete pore solution using electrochemical measurements. Saturated $\text{Ca}(\text{OH})_2$ solution (pH 12.5) was used as the simulated concrete pore solution for carrying out electrochemical measurements such as corrosion potential (E_{corr}), linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization (PDP)

measurements. The authors have used sodium nitrite (NaNO_2), sodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$), and benzotriazole (BTA) at the dosage of 0.25 mol.l^{-1} each as corrosion inhibitors, and NaCl (0.25 mol.l^{-1}) as the source of chloride ions. For electrochemical measurements, the three-electrode arrangement consisting of low-carbon rebar (diameter 14 mm and exposed area of 1 cm^2) as working electrode, saturated calomel electrode (SCE) as reference electrode, and platinum electrode as counter electrode was used. Before carrying out the electrochemical measurements, the steel specimens were immersed in saturated $\text{Ca}(\text{OH})_2$ solution (without admixed chloride) for 3 days to keep it passivated. The electrochemical measurements were carried out at different time intervals up to 936 hours. After completion of electrochemical measurements, Field emission scanning electron microscope (FESEM) equipped with energy dispersive X-ray analysis (EDXA) was carried out to study the microstructure and morphology of corrosion products formed on the steel. The pH of the simulated concrete pore solution was also monitored at regular intervals. The results indicated that to some extent, all the three corrosion inhibitors were capable of preventing corrosion of steel in simulated concrete pore solution. The addition of corrosion inhibitors decreased the pH of simulated concrete pore solution. The results obtained from LPR and EIS measurements showed that the corrosion inhibiting efficiency of inhibitors was in the order of $\text{BTA} > \text{NaNO}_2 > \text{Na}_3\text{PO}_4$. However, potentiodynamic polarization curves showed that NaNO_2 was more efficient in preventing pitting corrosion as compared to BTA followed by Na_3PO_4 . FESEM analysis indicated the formation of compact protective film on the steel surface in the presence of BTA.

Fei et al. [113] have carried out an experimental investigation to evaluate the corrosion inhibition performance of imidazoline quaternary ammonium salt (IQS) against corrosion of steel reinforcement in chloride contaminated simulated concrete pore solution using electrochemical measurements, and surface analysis of steel. Besides, the inhibition efficiency of IQS was also compared with sodium nitrite and alcohol–amine organic corrosion inhibitor. In this study, the chloride contaminated simulated concrete pore solution of pH 13.35 was prepared by dissolving calcium hydroxide (0.003%), sodium hydroxide (0.008%), potassium hydroxide (0.005%), and sodium chloride (3.5%) in deionized water. The IQS was added to the simulated concrete pore solution at the concentrations of 0%, 0.5%, 1%, and 2%. For comparison, simulated concrete pore solutions containing sodium nitrite (2%), and alcohol–amine organic corrosion inhibitor (2%) were also prepared. Steel specimens of 10 mm diameter (exposed area of 0.785 cm^2)

were used for potentiodynamic polarization (PD), electrochemical impedance spectroscopy (EIS), and potentiostatic polarization measurements. The steel samples were conditioned in the test solutions for different ages (1, 7, 14, and 28 days) before the potentiodynamic polarization (PD) and electrochemical impedance spectroscopy (EIS) measurements. For potentiostatic polarization measurement, steel samples were conditioned in simulated concrete pore solution without admixed chloride for 5 days followed by immersion in the relevant testing solutions, and the concentration of chloride in the testing solutions was progressively increased. At the end of electrochemical measurements, the surface of the steel specimens was investigated by scanning electron microscope (SEM) analysis, X-ray diffraction (XRD) analysis, and dynamic light scattering (DLS) measurement. Based on the obtained results from electrochemical measurements, the authors reported that the addition of IQS significantly improved the polarization resistance and pitting potential, and reduced the corrosion current density of steel reinforcement. Although, the steel immersed in 1% IQS showed slightly lower inhibition efficiency than the steel immersed in 2% sodium nitrite, but showed significantly higher inhibition efficiency as compared to 2% alcohol-amine organic corrosion inhibitor. Further, the effectiveness of IQS against steel reinforcement was higher at 1% concentration as compared to 0.5% and 2% concentrations. Surface analysis of steel indicated the formation corrosion products at 0.5% and 2% IQS concentration after 28 days of immersion in the test solution. However, in the presence of 1% IQS, no corrosion products were visible on the steel surface after 28 days of immersion in the test solution.

Haleem et al. [12] have studied the inhibition effect of benzotriazole and its derivatives such as 5-nitrobenzotriazole and 5-chlorobenzotriazole against steel reinforcement corrosion in saturated $\text{Ca}(\text{OH})_2$ solution contaminated with chloride ions. The test solution was prepared by adding different concentrations of NaCl (0.0001 M and 0.05 M) and corrosion inhibitors in saturated $\text{Ca}(\text{OH})_2$ solution of pH 12.9. The authors have performed potentiodynamic anodic polarization test on steel specimens of size 10 mm diameter and 50 mm length. Before carrying out the potentiodynamic anodic polarization test, the steel specimen was subjected to cathodic pretreatment for 20 minutes. The authors have also examined the steel surface through scanning electron microscope (SEM) and energy dispersion spectroscopy (EDS) analyses. From the obtained results, the authors observed that the inhibition efficiency of benzotriazole and its derivatives depends on the inhibitor type, concentrations of inhibitor, and chloride ion content. The inhibition efficiency of the

corrosion inhibitor increased in the order: 5-nitrobenzotriazole < benzotriazole < 5-chlorobenzotriazole. The inhibitors shift the critical pitting potential of steel to the noble direction thereby increasing the resistance to initiation of pitting corrosion. SEM and EDS analyses showed that benzotriazoles inhibited the pitting corrosion of steel through adsorption and/or precipitation of their chloro-complexes on the steel surface.

Nahali et al. [114] have carried out an investigation to study the inhibition effectiveness of phosphate based corrosion inhibitor against localized corrosion of steel reinforcement in chloride contaminated simulated concrete pore solution. Steel specimens of 6 mm diameter and exposure area of 0.28 cm² were used as test specimens for electrochemical measurements. Before electrochemical measurements, the steel specimens were immersed in 0.2% Ca(OH)₂ solution admixed with or without different concentrations (i.e., 1%, 3%, and 5%) of Na₃PO₄ for 7 hours for pretreatment. The steel specimens were immersed in 0.2% calcium hydroxide solution containing 5% Na₃PO₄ and different concentrations ([Cl⁻]/[OH⁻] molar ratio varying between 0 and 20) of NaCl during electrochemical measurements. The corrosion of steel specimen in test solutions was evaluated using cyclic polarization measurement followed by acoustic emission monitoring. Besides, the surface morphology and structure of steel specimen before and after addition of chloride was studied by scanning electron microscope coupled with energy dispersion spectroscopy, and X-ray diffraction analysis. From the obtained results, the authors reported that the treatment of steel in Ca(OH)₂+Na₃PO₄ solution results in the formation of a phosphate layer on the surface of steel reinforcement. In chloride contaminated solution with 5% Na₃PO₄, when the [Cl⁻]/[OH⁻] molar ratio was between 1 and 15, the phosphate layer was intact and totally covered the steel surface that effectively protects the steel from localized corrosion. When [Cl⁻]/[OH⁻] ratio was more than 15, the corrosion parameters indicated the breakdown of passivity, which leads to pitting corrosion of steel reinforcement. Further, the corrosion potential and polarization resistance decreased, and corrosion current density increased with increase in chloride concentration in the test solution.

Verbruggen et al. [6] have studied the effectiveness of different corrosion inhibitors against pitting corrosion (by chloride attack) and uniform corrosion (due to drop in pH) of steel specimens in simulated concrete pore solution. For pitting corrosion, simulated concrete pore solution of pH 13 was prepared by mixing potassium hydroxide (0.3 M), sodium hydroxide (0.1 M), calcium hydroxide (0.01 M), and sodium sulfate (0.002 M). In addition, different concentrations of NaCl such as (0, 0.14, 0.28, 0.56, and 1.4 M) were also

added in the simulated concrete pore solution. For uniform corrosion, carbonated concrete pore solution of pH 9 was prepared by mixing calcium carbonate (0.001 M) and sodium sulfate (0.002 M). Further, the authors have also prepared another concrete pore solution of pH 9 to simulate combination of carbonation and chloride attack by adding 0.014 M NaCl to the carbonated concrete pore solution. Corrosion inhibitors such as sodium molybdate dehydrate (Na_2MoO_4), cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3$), 2,5-Dimercapto-1,3,4-thiadiazole (DT), 2-Mercaptobenzothiazole (MBT), and 1H-benzotriazole (BTA) were added in the simulated concrete pore solution at the concentration of 10^{-4} M each. The authors have performed potentiodynamic polarization measurement on steel specimens of size 24 mm diameter and surface area of 450 mm^2 . Before the test, the steel specimens were exposed to electrolyte solution for 1 h to reach an equilibrium condition. After completion of potentiodynamic polarization measurement, the surface of the steel specimen was analyzed through optical microscopy, X-ray photoelectron spectroscopy (XPS), and scanning electron microscope (SEM) with energy and wavelength-dispersive X-ray spectroscopy (EDX and WDX). From the obtained results, the authors have observed that in the case of pitting corrosion, the inhibiting efficiency of corrosion inhibitor increased in the order: $\text{BTA} < \text{DT}$ and $\text{Ce}(\text{NO}_3)_3 < \text{Na}_2\text{MoO}_4 < \text{MBT}$, whereas in case of uniform corrosion, the inhibiting efficiency of corrosion inhibitors increased in the order: $\text{DT} < \text{MBT} < \text{Ce}(\text{NO}_3)_3 < \text{BTA} < \text{Na}_2\text{MoO}_4$. The results obtained from potentiodynamic polarization measurement and surface analysis of steel indicated that sodium molybdate dehydrate (Na_2MoO_4) performed best in three types of simulated concrete pore solutions. The authors concluded that Na_2MoO_4 is a possible and environmental-friendly inhibitor to prevent corrosion of steel reinforcement.

Yohai et al. [101] have experimentally studied the effectiveness of sodium biphosphate (Na_2HPO_4) as a corrosion inhibitor against corrosion of carbon steel exposed to carbonated solutions contaminated with chloride ions. Carbonated solution of pH 9 was prepared by mixing Na_2CO_3 (0.0015 mol/l) and NaHCO_3 (0.03 mol/l). To simulate a carbonated concrete pore solution contaminated with chloride ions, NaCl (0.1 mol/l) was added to the carbonated solution. Sodium biphosphate was used at the concentrations of 20, 60, and 100 mmol/l. The authors have obtained cyclic voltammograms, corrosion potential, polarization resistance, and electrochemical impedance spectra of carbon steel specimens having an exposed area of 0.503 cm^2 . The authors have also performed weight loss measurement on steel specimens having an exposed area of 5.67 cm^2 . Before performing the weight loss

measurement, the steel specimens were exposed to the test solution for a period of 42 days. In addition, Raman spectroscopy (after completion of electrochemical impedance spectroscopy (EIS) and weight loss measurements) and X-ray photoelectron spectroscopy (after 192 h of immersion in test solution) were also carried out on the steel specimens. From the obtained results, the authors reported that the addition of sodium biphosphate results in more positive corrosion potential of steel, and formation of more protective passive film over the steel specimen. With increase in sodium biphosphate concentration in the test solution, the inhibiting efficiency increased as the surface film over the steel became more protective to pitting corrosion.

Mansour et al. [115] have evaluated the efficiency of trisodium phosphate against corrosion of prestressing tendons in chloride contaminated concrete pore solution. For this purpose, ribbed steel wire of 4 mm diameter and 300 mm length was used as the test specimen. Saturated calcium hydroxide solutions admixed with and without 5% of trisodium phosphate (TSP) were used for electrochemical measurements. For chloride contamination, NaCl was added to the test solution at different concentrations to obtain $[\text{Cl}^-]/[\text{OH}^-]$ ratio varying between 0.2 and 15. In this study, open circuit potential (OCP) measurement, cyclic polarization (CP) curve measurement, electrochemical impedance spectroscopy, and acoustic emission (AE) test were carried out on the ribbed steel wire exposed to test solutions. In addition, the surface of the steel wire was studied by optical microscope and energy dispersive X-ray spectroscopy (EDX) analysis. From the obtained results of electrochemical measurements, the authors reported that the addition of trisodium phosphate enhanced the critical $[\text{Cl}^-]/[\text{OH}^-]$ ratio, and shifted both pitting potential and corrosion potential to more noble values indicating the anodic protection mechanism of trisodium phosphate. The results of acoustic emission and anodic polarization showed that incorporation of trisodium phosphate increases the time required to start prestressing tendons damage. The EDX analysis showed that phosphate ions form the compounds that block the anodic sites and delay the initiation of prestressed steel corrosion.

2.3 Effect of corrosion inhibitors on chloride ingress, binding of chloride ions and corrosion of steel reinforcement in cementitious composites

This section presents the reported research work on inhibition effect of different corrosion inhibitors against steel reinforcement corrosion in both cementitious composites and simulated concrete pore solutions subjected to chloride environment. Further, the effects of binder type, w/b, chloride concentration, and sulfate ion on the performance of corrosion

inhibitors are discussed in this section. In addition, the research work on the effect of corrosion inhibitors on hardened properties, chloride ingress, chloride binding, and microstructure of cementitious composites are also presented and discussed in this section.

2.3.1 Review of literature on effect of corrosion inhibitors in cementitious composites

Crentsil et al. [116] have studied the effect of carboxylic acids as corrosion inhibitors against steel reinforcement corrosion in chloride contaminated mortar. Mortar mixes were prepared using ordinary Portland cement at water: cement: sand proportion of 0.5: 1: 3. Sodium chloride (2.5% by weight of dry cement), and corrosion inhibitors (2.5% each by weight of dry cement) such as sodium malonate, calcium formate, calcium propionate, and calcium acetate were added to the mortar mixes during preparation. In this study, two sets of cylindrical mortar specimens: one embedded with three steel rods (each 6 mm in diameter and 75 mm in length) for electrochemical analysis, and the other without steel rod for chemical analysis were prepared from each mortar mix. The specimens were cured for 90 days, and during the curing period, ion chromatographic analysis, pH measurement, isothermal calorimetric measurement, and thermogravimetric analysis were carried out on the pore fluid extracted from the mortar specimens (without embedded steel bar). The linear polarization resistance measurement was carried out on reinforced mortar specimens. From the results of isothermal calorimetric measurement and thermogravimetric analysis, the authors reported that malonate works as a set retarder, whereas NaCl and calcium formate accelerated the hydration process of mortar. All the specimens that contained inhibitors and chloride showed higher pH values as compared to the specimens without inhibitors and chloride. The results of electrochemical analysis indicated that malonic acid was very effective even in the presence of 2.5% NaCl. However, other corrosion inhibitors showed an increase in corrosion rate and, the corrosion rate was at least two orders higher than malonate samples.

Gonzalez et al. [82] have carried out an experimental investigation to assess the ability of sodium nitrite (NaNO_2) against corrosive effect of chloride on steel reinforcement embedded in mortar mixed with artificial seawater. The authors have prepared two sets of mortar specimens of size 2 cm $\times$ 5 cm $\times$ 8 cm using Portland cement and four cement/sand ratios such as 1:1, 1:3, 1:6, and 1:8. Artificial seawater with a w/c of 0.4 or 0.6 was used in the preparation of mortar mix. Among the two sets of mortar specimens, one set of specimens contained two reinforcement steel rods of 8 mm diameter (as the working electrode) that were placed in symmetrical positions and a central stainless steel wire (as

counter electrode) to measure corrosion potential, and polarization resistance. The second set of specimens were prepared without any embedded electrode and were used in the nitrite and chloride leaching experiments. The authors have added NaNO_2 at two concentrations (2% and 4% by weight of cement) and in some specimens, CaCl_2 (2% by weight of cement) was added during preparation. After preparation, the specimens that contained steel reinforcement were immersed in distilled water, and artificial seawater for 30 days. The specimens without steel reinforcement were immersed in distilled water for 30 days. To identify alternative inhibitors as a substitute for nitrites, separate mortar specimens were prepared with eight other inhibitors (resorcinol, phloroglucinol, urotropin, sodium phosphate, potassium chromate, zinc oxide, sodium gluconate, and calcium gluconate) using only one cement/sand ratio of 1:3. The authors have used suitable ion-selective electrodes to quantify leaching of chlorides and nitrites. From the results, the authors have observed that the addition of 2% NaNO_2 to the mortar effectively counters the risk of corrosion of steel reinforcement embedded in mortar mixed with seawater. It was also observed that under immersion conditions, some dissolved nitrite in the mortar pores were leached. This indicated that reinforced concrete structures immersed in salty waters could not be permanently protected by corrosion inhibitors and the effectiveness of the protection was proportional to the quality of the concrete. The obtained results also indicated that the alternative corrosion inhibitors studied in the experimental investigation were not comparable to nitrite in terms of protective efficiency.

Tritthart and Banfill [117] have studied the influence of nitrite content and counter-ion type, age, water/cement ratio, and presence of chlorides on nitrite binding in cement pastes. For this purpose, cement pastes were prepared using normal Portland cement (PZ-375-EZ), a cement containing about 30% BFS (EPZ), a sulfate-resisting cement (HS-cement), and a British Portland cement (grade 42.5N) at w/c of 0.40, 0.50, 0.60 and 0.70. Two types of corrosion inhibitors namely sodium nitrite and calcium nitrite (each at the concentration of 0, 0.5%, 1%, 2%, and 3% by weight of cement), and two chloride salts i.e., NaCl and CaCl_2 (each at the Cl^- concentration of 1% by weight of cement) were added in the cement paste mixes during preparation. Pore solution was pressed out from the hardened cement pastes and used for the determination of free nitrite ion concentration by spectrophotometer; and hydroxyl ions and chloride ion concentrations by potentiometric titration. From the obtained results, the authors observed that the binding of nitrite ion was higher in the cement paste prepared from EPZ cement as compared to HS-cement followed by PZ-375-

EZ cement and the nitrite ions bound only at the early stages of hydration. The free nitrite concentration in pore solution decreased with an increase in w/c. The results also showed that nitrite, chloride, and hydroxyl ions compete with each other for the adsorption sites of cement paste, which indicates that the amount of free nitrite ions will be higher at higher chloride and/or hydroxide concentrations. The concentrations of free nitrite and hydroxyl ions in cement paste pore solution were less in case of calcium nitrite as compared to sodium nitrite. In cement pore solution, the $\text{Cl}^-/\text{NO}_2^-$ ratio was highest when sodium chloride and sodium nitrite were used, whereas the $\text{Cl}^-/\text{NO}_2^-$ ratio was lowest when calcium chloride and calcium nitrite were used.

Saraswathy et al. [118] have carried out an experimental study to design a composite corrosion-inhibiting admixture containing mineral and chemical admixtures and to evaluate its corrosion performance in concrete under macrocell corrosion conditions. In total, six concrete mixes were prepared using different combinations of OPC, fly ash, sodium hydroxide, sodium citrate, sodium stannate, and calcium oxide. Reinforced concrete specimens of size 279 mm × 152 mm × 114 mm and embedded with three mild steel bars (of size 10 mm diameter and 300 mm length) were prepared at w/c of 0.60 and using cement: sand: coarse aggregate proportion of 1: 3: 4.5 for macrocell corrosion studies. In addition, mortar cubes of w/c of 0.50 were prepared for 28 days compressive strength test. After 28 days of curing, the concrete specimens were subjected to 3% NaCl solution for 5 wetting drying cycles with one cycle consisting of 15 days of wetting followed by 15 days of drying. The authors have carried out open circuit potential measurement using saturated calomel electrode, and measured the macrocell current flow between anode and cathode using high-impedance voltmeter during the exposure period. At the end of exposure period, the corrosion rate of steel in different concrete mixes was determined by gravimetric weight loss measurement. The authors have also measured the pH and free chloride content of concrete mixes at the end of exposure. From the obtained results of macrocell corrosion study, the authors observed that the mixes containing composite corrosion-inhibiting admixture were more effective against corrosion of steel reinforcement as compared to OPC mix, and among the composite mixes, the mix containing all the inhibiting admixtures i.e., sodium hydroxide, sodium citrate, sodium stannate, and calcium oxide was most effective against corrosion. The composite mixes containing sodium hydroxide, sodium citrate, and sodium stannate decreased the corrosion rate of steel and increased the compressive strength of mortar. The pH measurement showed that the mixes containing

composite corrosion-inhibiting admixture preserve the alkalinity of concrete even in the presence of higher amount of chlorides. Further, all the mixes showed uniform free chloride content.

Rincon et al. [119] have compared the inhibition action of zinc oxide (ZnO) with calcium nitrite ($\text{Ca}(\text{NO}_2)_2$) against steel reinforcement corrosion in concrete. Besides, the effect of w/c on the performance of ZnO and $\text{Ca}(\text{NO}_2)_2$ as well as the effect of these inhibitors on physical–chemical properties of concrete were also investigated. In this study, concrete mixes were prepared using Type I Portland cement with tap water, and lake water (from Maracaibo Lake) at three w/c such as 0.45, 0.50, and 0.60. Zinc oxide and calcium nitrite were admixed at the concentrations of 2%, 3%, and 4% each (by weight of cement) during the preparation of specimens. In addition, concrete mix was also prepared with the mixture of two corrosion inhibitors each at the concentration of 2% by weight of cement. The concrete mixes were used to cast cylindrical concrete probes (of size 150 mm in diameter and 300 mm in length) with an embedded steel bar for electrochemical measurements, and without steel bar for compressive strength and porosity measurements. The probes containing $\text{Ca}(\text{NO}_2)_2$ were demoulded after 1 day of preparation, whereas the probes containing ZnO and a mixture of ZnO and $\text{Ca}(\text{NO}_2)_2$ were demoulded after 5, 8, and 11 days since zinc oxide is a set retarder. After completion of 28 days of curing, the cylindrical reinforced probes prepared with tap water were sprinkled with tap water for 30 min per day for 407 days. The cylindrical reinforced probes prepared with lake water were sprinkled with 0.3% NaCl solution for 30 min per day for 115 days followed by 3.5% NaCl solution up to 147th day. Thereafter, the specimens were placed in a salt chamber with NaCl at 5% concentration for 10.5 h/day for 500 hours. The corrosion of steel in concrete probes was monitored by half-cell potential, linear polarization resistance, and cyclic polarization measurements. Further, the chloride ion content at the rebar level was also measured as per ASTM D 512-65. Based on the obtained results, the authors reported the concrete containing $\text{Ca}(\text{NO}_2)_2$ showed higher compressive strength as compared to that containing ZnO, and the mixture of ZnO and $\text{Ca}(\text{NO}_2)_2$. The addition of ZnO reduced the concrete porosity and chloride content at rebar level. Further, the concrete containing ZnO always showed higher corrosion rate as compared to that containing $\text{Ca}(\text{NO}_2)_2$, which is probably due to the presence of Zn on the steel surface, which causes a new redox reaction. Despite higher corrosion rate of steel in concrete containing ZnO, the potential values and the cyclic polarization curves showed passivation of steel after more than two years of exposure to

chloride. However, after approximately 500 days of exposure to the saline medium, all the probes containing $\text{Ca}(\text{NO}_2)_2$ showed breakdown of the passive film on the steel reinforcement as indicated by the potential values. The authors concluded that concrete containing ZnO and its mixture with $\text{Ca}(\text{NO}_2)_2$ showed better performance against corrosion of steel reinforcement as compared to $\text{Ca}(\text{NO}_2)_2$. In the entire study period, the mixture of ZnO and $\text{Ca}(\text{NO}_2)_2$ each at 2% concentration showed best performance against steel reinforcement corrosion in concrete.

Kondratova et al. [120] have experimentally investigated the effectiveness of two corrosion inhibitors against corrosion of steel in uncracked and precracked reinforced concrete slabs exposed to natural marine environment for three years. The authors have prepared concrete slab specimens of size 55 mm × 230 mm × 300 mm embedded with two steel bars of 15.9 mm diameter as working electrode, and a stainless steel rod as counter electrode. The slab specimens were prepared using Type 10 Portland cement at w/c of 0.40. One organic corrosion inhibitor (OCI) at the concentration of 5 l/m³, and another calcium nitrite-based corrosion inhibitor (CNI) at the concentration of 25 l/m³ were admixed in the slab specimens during preparation. During preparation, in some of the slab specimens, rubber sheet was used to form cracks of sizes 0.2 mm, and 0.4 mm. All the slab specimens were cured for 28 days and then exposed to natural marine environment for three years. The corrosion activity of the reinforcing steel bars in concrete slabs was monitored annually using linear polarization resistance (LPR) technique. The authors have also performed conventional titration test to determine the water-soluble chloride-ion content profiles of uncracked and precracked slab specimens after 12 months of exposure. From the obtained results, the authors observed that after three years of natural marine exposure, all uncracked concrete specimens showed very low corrosion current density and no sign of corrosion was visible on the surface of the slabs. However, in the precracked concrete slabs, only after 12 months of exposure, the corrosion current density exceeded the moderate corrosion limit of corrosion and it was more in the slabs with higher crack width. It was also observed that OCI was more efficient than CNI in reducing corrosion rate in the uncracked concrete. In cracked concrete, both corrosion inhibitors were relatively inefficient against corrosion. The OCI corrosion inhibitor showed lower water-soluble chloride-ion content than CNI corrosion inhibitor.

Al-Amoudi et al. [1] have studied the performance of four types of corrosion inhibitors in concrete subjected to five different levels of contamination. The authors have prepared

plain and reinforced (centrally embedded with a steel bar of 12 mm diameter) cylindrical concrete specimens of 75 mm diameter and 150 mm height with Type V Portland cement at w/c of 0.45. Corrosion inhibitors namely calcium nitrite (2% and 4% by weight of cement), calcium nitrate (2%, 3%, and 4% by weight of cement), and two organic inhibitors i.e., CI1 (5 l/m³) and CI2 (1.2 kg/m³) were added during the preparation of concrete mixes. Four batches of specimens were prepared with washed aggregates and different levels of contamination such as 0.8% chloride, 0.8% chloride plus 1.5% SO₃, seawater, and brackish water. Another batch of specimens was prepared with unwashed aggregates. After curing, the reinforced cylindrical concrete specimens contaminated with 0.8% chloride, and seawater were subjected to 5% NaCl solution while those contaminated with 0.8% chloride plus 1.5% SO₃ were subjected to 5% NaCl + 3.11% Na₂SO₄ solution. The reinforced cylindrical concrete specimens contaminated with brackish water, and prepared with unwashed aggregates were immersed in brackish water. The plain cylindrical concrete specimens were used for determining the 28-day compressive strength, whereas the reinforced cylindrical concrete specimens were used for measuring the corrosion potential and corrosion current density (by linear polarization resistance measurement) of steel at different intervals up to 170 days of exposure. The compressive strength results showed that the concrete mixes containing corrosion inhibitors exhibited higher compressive strength than the control concrete mix. The corrosion studies indicated that all the four corrosion inhibitors were effective in delaying the initiation of steel reinforcement corrosion, and among the corrosion inhibitors, calcium nitrite was significantly efficient in delaying the corrosion initiation period in the concrete contaminated with chloride, chloride plus sulfate, and seawater. The results of corrosion current density indicated that all the four corrosion inhibitors were able to protect the passivity of steel bar. However, for better efficiency against steel reinforcement corrosion, calcium nitrite or calcium nitrate appeared to be the preferred corrosion inhibitor at the dosage between 3% to 4% for different levels of contaminations.

Montes et al. [121] have studied the influence of calcium nitrite based corrosion inhibitor and crack width of concrete on steel corrosion in high performance concrete subjected to simulated marine environment using linear polarization resistance measurement. Uncracked and precracked reinforced concrete slabs (of size 55 mm × 230 mm × 300 mm) were prepared using CSA Type 10L-SF low alkali Portland cement, Class F fly ash of three different contents (0%, 20%, and 40%), air entraining admixture, a set retarder,

superplasticizer, and three w/c (0.29, 0.37, and 0.45). Cracks of width 0.25 mm or 0.50 mm were formed in the reinforced concrete slabs using rubber sheet during preparation. Calcium nitrite (CNI) was admixed at the dosage of 0, 12.5, and 25 l/m³ during the preparation of concrete mixes. Two steel bars of size 15 mm diameter and 260 mm length as working electrode, and one stainless steel bar as counter electrode were embedded inside the slab specimens. After preparation, the specimens were subject to wetting and drying cycles with two complete cycles performed within 24 hours in simulated marine environment (i.e., exposure in simulated salt water solution prepared as per ASTM D 1141-80) for 1 year. The corrosion activity of steel in concrete slab specimens was monitored at regular intervals by linear polarization resistance (LPR) measurement. The results obtained from LPR measurement indicated that the cracking of the concrete strongly affects the rate of corrosion as the steel in uncracked concrete slabs was in passive condition, whereas the steel in pre-cracked slabs was in moderate to high corrosion condition. The addition of fly ash was effective in decreasing the corrosion of steel in uncracked and the slab specimens with 0.25 mm crack. However, in slab specimens with 0.50 mm crack, the influence of fly ash in reducing the steel corrosion was not visible. It was also found that the corrosion protection of calcium nitrite against steel reinforcement corrosion depends on the presence of fly ash and the quality of concrete. The use of calcium nitrite (added at 12.5 l/m³) in good quality concrete (w/c = 0.29 or 0.37) with 20% fly ash appeared to be the desirable approach to minimize the effect of chloride induced corrosion of steel reinforcement.

Schutter and Luo [122] have experimentally investigated the effect of four corrosion inhibitors on properties of fresh concrete such as density, workability, and air content; and on the properties of hardened concrete such as compressive strength, bending tensile strength, splitting tensile strength, and Young's modulus. In total, 10 concrete mixes were prepared with w/c of 0.45 using Portland cement (CEM I 42.5 R), blast furnace slag cement (CEM III/A 42.5 LA), and four types of corrosion inhibitors (added during preparation of concrete) such as calcium nitrite based corrosion inhibitor (5 l/m³), amino and ester based corrosion inhibitor (5 l/m³), a combination of amino alcohols, inorganic and organic corrosion inhibitor (12.25 kg/m³), and a migrating corrosion inhibitor (0.5 kg/m³). The authors obtained the concrete density by determining the weight of fresh concrete, workability by slump test, air content using pressure type air-meter; and mechanical properties (at the age of 3, 7, and 28 days) by performing compressive strength test, bending tensile strength test and splitting tensile strength test. Concrete cube specimens of side

length 158 mm were used for compressive strength test, whereas beam specimens of size 150 mm × 150 mm × 600 mm were used for bending tensile strength test. The splitting tensile strength was performed on the two halves of the broken specimens obtained after bending test. To obtain the Young's modulus of concrete (at the age of 3, 7, and 28 days), cylindrical specimens having diameter 150 mm and height 300 mm were used. From the obtained results, the authors observed that the calcium nitrite based corrosion inhibitor increased the workability, and early age compressive strength and bending tensile strength of concrete for both cements. The ultimate compressive strength remained unchanged for Portland cement concrete and decreased for blast furnace slag cement concrete. The addition of calcium nitrite based corrosion inhibitor decreased the 28-day bending tensile strength in case of Portland cement concrete, and increased in case of blast furnace slag cement concrete. The effect of amino and ester based inhibitor on workability was not clear while amino alcohol based inhibitor increased the workability of concrete. The amino and ester based inhibitor, and amino alcohol based inhibitor decreased the compressive strength, bending tensile strength and splitting tensile strength of concrete for both types of cement at all ages. The migrating corrosion inhibitor decreased the early age compressive strength, while the ultimate compressive strength seems to be improved for both types of cement. Besides, there was no significant influence of corrosion inhibitors on air content and Young's modulus of concrete.

Sideris and Savva [123] have carried out an experimental investigation to evaluate the influence of calcium nitrite on corrosion of steel embedded in mortar contaminated with chloride as well as its effect on chloride binding capacity of mortar. In this study, mortar mixes were prepared using two Portland cements i.e., Type 1 Portland cement (NPC) and Type V sulfate resistant cement (SR), and 12 blended cements. The blended cements were made in laboratory by grinding Portland clinker, gypsum, and pozzolanic materials at different proportions. The pozzolanic materials used were natural pozzolan i.e., Milos' Earth (ME) at 10% and 30%, silica fume at 10% and 15%, and three lignite fly ashes namely Megalopoli's fly ash (MFA) at 10% and 30%, Ptolemaida's fly ash (PFA) at 10% and 30%, and Ptolemaida's treated fly ash (PtFA) at 30%, 40%, and 50%. In addition, one commercially available blended cement (CEM II32.5N) was also used in the preparation of mortar mixes. Calcium nitrite was added at the dosage of 20 l/m³ during preparation of mortar mixes. Mortar cylinders of size 40 mm diameter and 100 mm length with or without a centrally embedded 10 mm diameter steel bar were prepared using cementitious material:

aggregate ratio of 1:3, and water/cementitious material ratio of 0.45 for carbonation and chloride-induced corrosion measurements. After 28 days of curing, the specimens were divided into two sets, where one set was used for carbonation measurement, and the other set of specimens were partially immersed in 5% NaCl solution for 2 years, and used for half-cell potential and gravimetric weight loss measurements as well as for chemical analysis (measurement of total chloride content, free chloride content and nitrite content). Mortar prisms of size 40 mm × 40 mm × 160 mm were also prepared for determination of compressive strength at the age of 7, 14, 21, 28, 60, 90, and 112 days. The results showed that the blended cement mixes exhibited better compressive strength than Portland cement mixes at all ages. The addition of calcium nitrite slightly increased the compressive strength of mortar mixes. Results of half-cell potential measurement indicated that calcium nitrite increased the corrosion resistance in all mortar mixes and the protection offered by calcium nitrite was strongly dependent on the type of cement used. The best results against steel reinforcement corrosion were obtained in case of combined use of calcium nitrite, and 30% ME, MFA, PtFA, and 10% silica fume. The beneficial effect of calcium nitrite against steel corrosion was also confirmed by the gravimetric weight loss measurements performed after 2 years of immersion in 5% NaCl solution. It was also observed that the carbonation depth of all mixtures was reduced or remained same when calcium nitrite was used. The results of chloride analysis showed significant variations in the free chloride content of mortar mixes, which was attributed to different chloride binding properties of the cementitious materials used in the preparation of mortar mixes. The results of total chloride content indicated that the addition of calcium nitrite did not influence the chloride permeability of mortar mixes. Further, the concentration of nitrite was higher in the mixes containing silica fume, whereas it was lower in the mixes prepared from NPC, Type V sulfate resistant cement, CEM II32.5N cement, and 30% PFA.

Civjan et al. [124] have studied the effectiveness of calcium nitrite, silica fume, Class F fly ash, ground granulated blast furnace slag (BFS), disodium tetrapropenyl succinate (DSS), and the combinations of these admixtures in reducing the corrosion of steel reinforcement in concrete. In this study, concrete mixtures were prepared using Type I/II Portland cement (ASTM C 150-02) and admixtures at different dosages such as calcium nitrite at 14.8 l/m³, silica fume at 6% cement replacement (by weight), fly ash at 15% cement replacement (by weight), BFS at 25% cement replacement (by weight), and DSS at 1/2% by weight of cement at water-to-cementitious material ratio (w/cm) of 0.40. In total,

14 concrete mixes were prepared including control mix, a mix containing single admixture, a mix containing double and triple combinations of admixtures, and two mixes containing double admixtures but at w/cm of 0.47. The concrete mixes were used to cast non-cracked and pre-cracked slab specimens of size 180 mm × 305 mm × 305 mm with embedded steel bars. The 28-day compressive strength of concrete mixes was determined using cylindrical specimens. After a minimum of eight weeks of curing at ambient laboratory condition, the sides of the slab specimens were sealed with epoxy to prevent ingress of chloride ions. After that, the specimens were subjected to a ponding sequence consisting of 24-week cycles. For the first 12 weeks, the specimens were ponded with 15% NaCl solution for 4 days followed by drying for three days. In the final 12 weeks, the specimens were continuously ponded with 15% NaCl solution. The 24-week cycles repeated for a total of 108 weeks. The corrosion activity of slab specimens was monitored by visual inspection, half-cell potential measurement, macrocell corrosion measurement, and destructive evaluations (by visual assessment of steel surface and determination of water-soluble chloride content). The obtained results indicated that in non-cracked concrete, calcium nitrite as a single admixture provided excellent protection against steel reinforcement corrosion however, in the presence of cracking, it was not particularly effective. The best protection against steel reinforcement corrosion in concrete was provided by the triple combinations of calcium nitrite, silica fume, and either fly ash or BFS, as well as by the double combination of calcium nitrite and BFS. It was also observed that all these mixtures resulted in higher compressive strength than control concrete. Further, the addition of DSS showed superior performance for corrosion prevention as compared to other admixtures. However, DSS lowered the compressive strength of concrete.

Ann et al. [11] have investigated the corrosion inhibition effect of commercially available calcium nitrite-based corrosion inhibitor (ACI) by measuring corrosion potential and corrosion rate of steel in chloride contaminated mortar. In addition, the effect of calcium nitrite-based corrosion inhibitors i.e., ACI, DCI, and NR 1200 on compressive strength and chloride permeability (as per ASTM C1202) of concrete were also evaluated. Cylindrical mortar specimens (of size 75 mm diameter and 150 mm length) with a centrally embedded steel bar of 9.5 mm diameter were prepared using cement (OPC): water: sand proportion of 1: 0.50: 2.13 with four levels of admixed ACI inhibitor (i.e., 0, 3, 6, and 12 l/m³) and five levels of admixed chloride (i.e., 0, 1.5, 3, 6, and 12 kg/m³) for corrosion tests. The mortar specimens were cured for 28 days and then partially immersed in 0.5 M sodium

chloride solution for 24 h to obtain chemical stability. Cylindrical concrete specimens of size 100 mm diameter and 200 mm length for compressive strength test at the age of 7, 28, 60, and 900 days, and concrete disk of size 100 mm diameter and 50 mm thickness for rapid chloride permeability test were prepared using OPC at a w/c 0.50 and different concentrations (such as 0, 3, 6, and 12 l/m³) of corrosion inhibitors (ACI, DCI, and NR 1200). Setting time of mortar extracted from the concrete mixes admixed with ACI inhibitor was also determined. The test results indicated that for all the corrosion inhibitors, the compressive strength of concrete mixes admixed with corrosion inhibitor was higher than the control mixes at early ages (i.e., up to 60 days). However, at 900 days, the compressive strength of concrete mixes admixed with corrosion inhibitor slightly reduced as compared to control mix. The setting time of concrete mixes decreased with an increase in the dosage of corrosion inhibitor whereas the compressive strength of concrete did not depend on the dosage of corrosion inhibitor. Corrosion test results showed that the corrosion rate was reduced due to the addition of corrosion inhibitor (ACI) at all levels of chloride ions in the mortar. The chloride threshold level increased with an increase in the dosage of corrosion inhibitor. The chloride permeability test results indicated that the addition of corrosion inhibitor increased the total charge passed through the concrete specimens as compared to the control specimen.

Song and Saraswathy [92] have studied the effectiveness of sodium nitrite, zinc oxide, monoethanolamine, diethanolamine, and triethanolamine against corrosion of steel reinforcement in concrete using electrochemical techniques. Concrete mixes were prepared using ordinary Portland cement at cement: sand: coarse aggregate proportion of 1:1.29:3.90 (by mass) and water-to-cement ratio (w/c) of 0.53. The corrosion inhibitors were admixed at the concentrations of 1%, 2%, and 3% each by weight of cement. In addition, the combination of sodium nitrite and zinc oxide was also used as corrosion inhibitor. Concrete discs of size 100 mm in diameter and 50 mm in thickness were used for rapid chloride ion penetration test (RCPT). Furthermore, cylindrical concrete specimens of size 50 mm diameter and 100 mm height with a centrally embedded steel bar (of size 10 mm diameter and 100 mm length) were prepared for open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization resistance measurements. In addition, cylindrical specimens of size 55 mm diameter and 60 mm height with a centrally embedded steel bar (size: 12 mm diameter and 50 mm length) were also prepared for gravimetric weight loss measurement. After 28 days of curing, the

reinforced specimens were subjected to alternate wetting and drying cycles with one cycle consisting of 7 days wetting in 3% NaCl solution followed by 7 days drying for 180 days. The RCPT results showed that the addition of corrosion inhibitors reduced the permeability of concrete. In all the electrochemical studies, zinc oxide and the combination of sodium nitrite and zinc oxide showed better performance against corrosion as compared to other corrosion inhibitors. The obtained results also showed that the optimum percentage addition of corrosion inhibitor was 2% by weight of cement.

Gurten et al. [125] have investigated the influence of thiosemicarbazide (TSC) on corrosion resistance of steel reinforcement as well as on the compressive strength of concrete. For this purpose, two groups of concrete mixes were prepared: one group with distilled water as mixing water, and the other group with 0.1 M chloride solution as mixing water using w/c of 0.50. Thiosemicarbazide was added at the concentration of 1×10^{-3} M in one mix of each group during the preparation of specimens. The concrete mixes were used to prepare cylindrical specimens of size 40 mm in diameter and 70 mm in height with a centrally embedded steel bar (size: 10 mm diameter and 50 mm length) for electrochemical test and cubes of size 150 mm for compressive strength. The cube and cylindrical concrete specimens were cured for 28 days, and 60 days respectively in different external solutions such as distilled water, 0.1 M NaCl solution, and solution containing 0.1 M NaCl + 1×10^{-3} M TSC. The effectiveness of thiosemicarbazide against corrosion was monitored by corrosion potential, linear polarization resistance (LPR), and AC impedance spectroscopy measurements. Based on the obtained test results, the authors have reported that the addition of thiosemicarbazide increased the compressive strength of concrete by 20% to 25% as compared to the concrete without thiosemicarbazide. Further, the use of thiosemicarbazide (TSC) in mixing water or external solution resulted in less negative corrosion potential and significantly higher polarization resistance of steel reinforcement in concrete than that without TSC. Besides, the addition of TSC in concrete with distilled water was more effective in reducing the corrosion rate as compared to that where TSC was added in concrete with chloride.

Reou and Ann [126] have experimentally investigated the effect of calcium nitrite-based inhibitor on corrosion inhibition of steel reinforcement as well as on strength development of blended concretes. Concrete mixes were prepared using ordinary Portland cement (OPC), OPC partially replaced by pulverized fuel ash (PFA) at 30% by weight of binder, and OPC partially replaced by ground granulated blast furnace slag (GGBS) at 65% by

weight of binder at water to binder ratio of 0.45. The corrosion inhibitor was added at three concentrations such as 1%, 2%, and 3% by weight of binder during the preparation of concrete mixes. Compressive strength test was carried out on cylinders of size 200 mm length and 100 mm diameter at the age of 7, 28, 56, 91, 180, and 365 days. Further, the rate of chloride transport through concrete containing calcium nitrite was studied by rapid chloride penetration test (as per ASTM C1202-91), and chloride diffusion test. For rapid chloride penetration test, concrete disc of size 50 mm in thickness and 100 mm in diameter was used. For corrosion and chloride diffusion tests, concrete cube specimens of size 150 mm with a centrally embedded steel bar were prepared. After 24 hours of preparation, the cube specimens were demoulded and cured in a polythene film to avoid leaching out of hydration products. A concrete slice on one side of the specimen parallel to the steel bar was sawn off thereby reducing the thickness of concrete cover to 10 mm for exposure to chloride solution. The remaining cast surfaces of the cube specimens were sealed with epoxy coating to facilitate one directional diffusion of chloride ions. The specimens were exposed to 4 M sodium chloride solution, and the time to corrosion initiation and galvanic current of steel were measured. After 15-30 days of corrosion initiation, the acid soluble chloride content at different depths intervals from the exposure surface of cube specimens was determined by potentiometric titration. The chloride contents were used for determination of apparent chloride diffusion coefficient using Fick's second law of diffusion. Based on the obtained results, the authors reported that the addition of calcium nitrite showed marginal effect on the compressive strength of concrete. Among the binders, the mix prepared from OPC showed highest compressive strength followed by 30% PFA and 65% GGBS. The replacement of OPC by PFA and GGBS lowered the diffusion of chloride ions through concrete. Further with an increase in the concentration of corrosion inhibitor, the diffusivity of chloride ions in concrete made with 30% PFA, and 65% GGBS increased. The inhibitor addition was very effective in increasing the resistance to chloride-induced corrosion for all binders. The authors also reported that the chloride threshold level for corrosion increased with an increase in calcium nitrite content in concrete.

Mehthel et al. [127] have evaluated the performance of some generic and proprietary corrosion inhibitors in reducing the corrosion rate of steel reinforcement in chloride-contaminated silica fume cement concrete. Four batches of cylindrical concrete specimens of size 75 mm diameter and 150 mm height with a centrally embedded steel bar of 12 mm diameter were prepared using Portland cement, silica fume, and four types of corrosion

inhibitors such as i) calcium nitrate (CI-1), a generic corrosion inhibitor, ii) CI-2, a calcium nitrite-based proprietary corrosion inhibitor, iii) CI-3, a proprietary migratory corrosion inhibitor, and iv) CI-4, a proprietary organic corrosion inhibitor. The concrete mixes were prepared at a w/c of 0.40. The corrosion inhibitors CI-1, CI-2, and CI-4 were added during the preparation of concrete mixes at the dosage of 4% by weight of cement, 10 l/m³ of concrete, and 5 l/m³ of concrete respectively. The corrosion inhibitor CI-3 was applied on the surface of cylindrical reinforced concrete specimens after 21 days of curing. The concrete mixes were contaminated with different concentrations of chloride such as 0.4%, 1%, and 2% by weight of cement. The specimens were divided into two groups. One group of the specimens was subjected to wetting-drying cycles (30 min wetted twice in a week and then dried) for 20 months and used to measure corrosion potential and corrosion current density. The second group of specimens was partially immersed in 5% sodium chloride solution and steel reinforcement corrosion was accelerated by impressing an anodic potential of 2 V for the impressed current technique. The authors concluded that the corrosion initiation time of steel reinforcement and time required for the formation of crack in concrete decreased with an increase in chloride concentration. The use of corrosion inhibitors increased the corrosion initiation time and time to cracking of concrete specimens. The corrosion inhibitors effectively decreased the corrosion current density of steel reinforcement and the best performance was shown by the inhibitor CI-4 followed by the inhibitors CI-3, CI-1, and CI-2.

Bastidas et al. [128] have compared the performance of three soluble phosphates such as sodium monofluorophosphate ($\text{Na}_2\text{PO}_3\text{F}$, MFP), disodium hydrogen phosphate (Na_2HPO_4 , DHP), and trisodium phosphate (Na_3PO_4 , TSP) as corrosion inhibitors against steel reinforcement corrosion in cement paste and mortar. The authors have prepared ordinary Portland cement (OPC) paste specimens of size 10 mm × 10 mm × 60 mm at with w/c of 0.35, and OPC mortar specimens of size 20 mm × 55 mm × 80 mm with water: sand: cement proportion of 0.5: 3: 1 (by mass). In the mortar specimens, two carbon steel bars of 8 mm diameter as working electrode were symmetrically embedded, and a stainless steel cylinder of 50 mm diameter as counter electrode was inserted in the central position. The corrosion inhibitors were used in two different ways: by immersion of specimens in aqueous solutions containing the inhibitors (at concentration of 0.2 M), and by addition of the inhibitor powders (3% by weight of cement) during the preparation of specimens. The cement paste specimens were used for wavelength-dispersive electron microprobe analysis (EMPA) and

X-ray diffraction (XRD) analysis. Further, diffusion experiment was carried out on the paste specimens exposed to 0.2 M phosphate solutions (i.e., MFP, DHP, and TSP). The mortar specimens were used to carry out electrochemical corrosion tests such as electrochemical corrosion potential, and linear polarization resistance measurements. The results of EMPA analysis showed that the P_2O_5 content for specimens admixed with MFP, DHP, and TSP were 0.47%, 0.45%, and 0.43% respectively. The specimens exposed to phosphate solutions showed lower P_2O_5 content as compared to that admixed with phosphates. The results of XRD analysis indicated that the presence of small amount of phosphates did not change the crystalline phases of cement paste, as no new formation of crystalline phase was observed in the cement pastes containing phosphate with respect to the cement paste without phosphates. Further, the diffusion rate of phosphate compounds decreased in the order of MFP > DHP > TSP. From the corrosion tests results, it was observed that both the admixture and migrating corrosion inhibitors were equally effective in corrosion inhibition. The corrosion inhibition efficiency of phosphates as migrating corrosion inhibitor decreased in the order of MFP > DHP > TSP. For specimens admixed with corrosion inhibitor, DHP showed the best corrosion inhibiting behavior among the tested phosphate compounds.

Fayala et al. [129] have carried out an experimental study to evaluate the inhibition efficiency of sodium nitrite (SN) and diethanolamine (DEA) to protect galvanized steel reinforcement embedded in mortar against corrosion, and their effect on properties of mortar before and after exposure to chloride environment. The authors have prepared prismatic mortar specimens of size 40 mm × 40 mm × 160 mm with or without a centrally embedded galvanized steel bar using cement/sand ratio 0.33 and w/c of 0.60. The inhibitors i.e., sodium nitrite at the dosage of 2% by weight of cement, and diethanolamine at the dosage of 3.5 l/m³ of mortar were added to the mixing water during the preparation of mortar mixes. The specimens were cured for 28 days in distilled water and then one set of these specimens were subjected to alternate wetting and drying cycles (3 days wetting and 3 days drying) in 3% sodium chloride solution in order to accelerate chloride penetration. The wetting and drying cycles were continued up to 7 cycles for unreinforced specimens, and up to 12 cycles for reinforced specimens. The authors have performed electrochemical impedance spectroscopy (EIS), mercury intrusion porosimetry, impedance spectroscopy (for mortar permittivity and mortar resistivity), and differential scanning calorimetry (DSC). The obtained polarization resistance value showed that diethanolamine improved

the corrosion resistance of galvanized steel in the mortar exposed to 3% NaCl solution whereas sodium nitrite accelerated the corrosion process. From the calorimetry investigation (DSC curves), generally the inhibitors did not influence the cement hydration, however, there was a modification in the stages of C–S–H dehydration especially due to the addition of DEA. The results of mercury intrusion porosimetry test revealed that the addition of corrosion inhibitors influenced the microstructure and pore distribution of mortar. The mortar mix admixed with diethanolamine (DEA) showed lower total porosity as compared to that admixed with sodium nitrite. The addition of diethanolamine (DEA) decreased the total porosity of mortar by blocking the pores through a gel formation, which resulted in reduction in chloride ingress in the mortar.

Okeniyi et al. [84] have investigated the effect of potassium chromate and sodium nitrite as inhibitors on the corrosion degradation of steel reinforcement in sulphuric acid and sodium chloride environment. The authors have prepared concrete blocks of size 160 mm × 100 mm × 100 mm with a centrally embedded steel bar (size: 10 mm diameter and 160 mm length) using ordinary Portland cement at w/c of 0.44, and cement, sand and gravel mix proportion of 1:2:4. The specimens were admixed with sodium nitrite and potassium chromate at different concentrations (varying from 1.5 gm to 9 gm by mass) and NaCl of concentration 0.1 M during preparation. After preparation, the specimens were divided into two sets, and the first set of specimens was partially immersed in 0.5 M dilute sulphuric acid (H₂SO₄) medium to simulate microbial (or sewage) environment. The second set was partially immersed in 3.5% sodium chloride (NaCl) medium to simulate marine/saline environment. The authors have measured the open circuit potential of steel specimen in concrete using Cu/CuSO₄ electrode during an exposure period of 32 days. They have also performed compressive strength test at the end of exposure period. From the obtained results of corrosion potential, the authors have observed that in the acidic medium, concrete admixed with 4.5 g potassium chromate exhibited optimum inhibition effectiveness with good improvement in compressive strength. The performance of sodium nitrite in acidic medium against steel reinforcement corrosion was very poor. In the saline medium, the concrete admixed with potassium chromate showed poor performance against corrosion of steel. However, the concrete admixed with 7.5 g sodium nitrite exhibited optimal inhibition performance against steel reinforcement corrosion in saline medium with reduction in compressive strength of concrete.

Shi and Sun [130] have carried out an experimental study to evaluate the effect of phosphate based inhibitor on chloride induced steel reinforcement corrosion in mortar. Prismatic mortar specimens of size 40 mm × 40 mm × 160 mm were prepared using ordinary Portland cement with cement to sand ratio (c/s) of 0.67 by mass, and water/cement ratio (w/c) of 0.53 by mass. Two types of steel bar such as pre-rusted steel bar, and as-received steel bar of diameter of 8 mm were embedded centrally in the mortar specimens keeping the cover depth as 16 mm. Two types of corrosion inhibitors such as NaNO₂ (SN) and Na₃PO₄·12H₂O (SP) were added during mixing and the concentration of each inhibitor was 0.4 M per kg cement. After 28 days of curing, the specimens were exposed to 3.5% NaCl solution for a period of 360 days. The mechanical method included determination of flexural strength and compressive strength of prismatic mortar specimens without steel reinforcement at early curing stage (28 days) and at long-term exposure to atmospheric environment (360 days). The electrochemical methods included linear polarization resistance (LPR) measurement, electrochemical impedance spectroscopy (EIS) measurement, and cyclic polarization (CP) measurement. The authors have also carried out environmental scanning electron microscopy (ESEM) to study the microstructure variations of steel-mortar interface. The obtained results of LPR and EIS indicated that at same concentration by weight of cement, nitrite was more effective in reducing the uniform corrosion rate of steel reinforcement than phosphate. However, according to cyclic polarization (CP) measurement, the probability of pitting corrosion was slightly lower for phosphate as compared to nitrite. From the environmental scanning electron microscopy study, the authors suggested that the corrosion inhibition mechanism of phosphate in mortars was dependent on a dual effect occurring at the steel–mortar interface, i.e., reaction with steel against chloride-induced corrosion, and formation of precipitates with hydration products of cement. Further, the pre-rusted steel bar showed a slightly higher corrosion rate than as-received steel bar. The results of flexural strength and compressive strength indicated that nitrites tend to be a strength enhancer, while phosphates seem to exhibit little effect on strength development of mortar.

Bastidas et al. [83] have carried out an experimental study on the performance of three phosphate compounds namely sodium monofluorophosphate (MFP), disodium hydrogen phosphate (DHP), and trisodium phosphate (TSP) against corrosion of steel rebar in mortar exposed to 3% NaCl solution. Mortar specimens of size 20 mm × 55 mm × 80 mm and embedded symmetrically with two 8 mm diameter carbon steel bars as working electrode

were prepared using OPC with water: sand: cement proportion of 0.5: 3: 1. The corrosion inhibitors were applied in two ways such as and migrating corrosion inhibitor (MCI), and admixture corrosion inhibitor (ACI). In case of MCI, the mortar specimens were prepared without admixed corrosion inhibitors and cured for 28 days. After curing, the specimens were fully immersed for 28 days in 0.2 M aqueous solution of each corrosion inhibitor and then were immersed in 3% NaCl aqueous solution. The corrosion behavior of steel bars in mortar specimens was monitored up to 70 days using electrochemical corrosion potential (E_{corr}) and linear polarization resistance (LPR) techniques. In case of ACI, the mortar specimens were admixed with MFP, DHP, or TSP at the dosage of 3% each by weight of cement during preparation. Then, the specimens were cured for 28 days and then immersed in 3% NaCl aqueous solution. The corrosion behavior of steel bars in mortar specimens was monitored up to 70 days. The results showed that the best corrosion inhibition efficiency in both MCI and ACI specimens was shown by the MFP compound and the order of inhibition efficiency was $\text{MFP} > \text{DHP} > \text{TSP}$. The inhibition efficiency indicated that DHP and to some extent TSP are good alternatives to the expensive MFP compound for use as migrating corrosion inhibitors. The MFP and DHP compounds showed corrosion current density (I_{corr}) values close to the passive state of steel thereby indicating their ability to inhibit steel corrosion in mortar. The corrosion inhibition effect of all the three phosphate compounds was higher for MCI specimens as compared to ACI specimens.

Nahali et al. [131] have studied the effect of Na_3PO_4 on the mechanical properties, and corrosion behavior of steel reinforcement in mortar exposed to 3% NaCl solution. For electrochemical measurements, cylindrical mortar specimens of size 30 mm diameter and 60 mm height with a centrally embedded steel bar (size: 6 mm diameter and 70 mm in length) were prepared using ordinary Portland cement with water-to-cement ratio of 0.5 and cement-to-sand ratio of 0.3. During the preparation of mortar mixes, Na_3PO_4 was added at the concentration of 0.3 mol/kg of cement. Using the same composition of mortar, the authors have also prepared prismatic specimens of size 40 mm $\times$ 40 mm $\times$ 160 mm for 28-day flexural strength test, 28-day compressive strength test, elasticity modulus measurement, scanning electron microscopy (SEM) analysis, and X-ray diffraction (XRD) analysis. The electrochemical measurements of cylindrical reinforced mortar specimens included the determination of corrosion potential, electrochemical impedance diagram, and polarization curves. Sodium chloride (3%) solution was used as the corrosion medium for this investigation. From the obtained test results, the authors have observed that the addition

of phosphates in mortar mixes has no significant effect on flexural strength whereas it decreased the compressive strength of mortar specimens by 14% as compared to the control specimens. The elasticity modulus results indicated that Na_3PO_4 slows the kinetics of cement hydration and acts as a retarder on the setting time of mortar. The results of SEM and XRD analyses showed the formation of phosphate based compounds such as acidic hydrated pyrophosphate and brushite in the mortar admixed with Na_3PO_4 . The results from electrochemical measurements showed that the addition of Na_3PO_4 efficiently improves the passivity of steel, reduces the corrosion rate and protects the steel against localized corrosion through the formation of a passive layer over the steel surface.

Yohai et al. [96] have carried out an experimental investigation to evaluate the effectiveness of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ as corrosion inhibitor for steel reinforcement in mortar contaminated with chloride ions. Three mortar mixes (Mix A, Mix B, and Mix C) were prepared using Portland cement with water-to-cement ratio of 0.6 and sand-to-cement ratio of 3. The mix A had no admixed chlorides; Mix B was contaminated with 1% chloride ion (by weight of cement); and Mix C was admixed with 1% chloride ion (by weight of cement) and 7% $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (by weight of cement). Two types of cylindrical mortar specimens (of size 28 mm diameter and 80 mm height) i.e., one with a centrally embedded steel bar of 8 mm diameter and the second one without steel bar were prepared from each mortar mix. The reinforced cylindrical mortar specimens were exposed to 0.5 mol/l NaCl solution up to an exposure period of 720 days. Corrosion potential, polarization resistance, polarization curves, and electrochemical impedance spectroscopy measurements were carried out on the reinforced mortar specimens. Raman spectra were collected on at least five representative spots, either on steel or on mortar after subjecting the electrodes to anodic polarization curves. Further, the specimens without steel reinforcement were used to determine the porosity of mortar. In addition, the specimens (without steel reinforcement) prepared from Mix A were immersed in 0.5 mol/l of NaCl solution for a period of 360 days and total chloride ion content was measured followed by determination of chloride diffusion coefficient of mortar. From the obtained results, the authors reported that $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ behaved as mixed type corrosion inhibitor and showed an inhibiting efficiency higher than 95% (as per the results obtained from electrochemical impedance spectroscopy), and higher than 70% (as per the results obtained from linear polarization measurement) against corrosion over the entire exposure period of 720 days. From the obtained results of Raman analysis, the authors concluded that phosphate prevents iron

dissolution and delays the diffusion of oxygen in mortar through the formation of a thin and compacted corrosion products layer over the steel surface. In addition, phosphate precipitates as calcium phosphate and hinders the diffusion of oxygen and chloride.

Nahali et al. [25] have experimentally investigated the influence of phosphate based corrosion inhibitor i.e., Na_3PO_4 on chloride ion diffusion and steel reinforcement corrosion in mortar. For this purpose, mortar mixes with and without admixed Na_3PO_4 were prepared using Type II PC-32.5 cement at water-to-cement ratio (w/c) of 0.5 and cement-to-sand ratio (c/s) of 0.3. The Na_3PO_4 was added to the mortar at the concentration of 0.3 mol/1kg of cement during preparation. The authors have prepared cylindrical mortar specimens of size 60 mm in diameter and 15 mm in thickness. For this study, a specific diffusion cell consisting of two compartments i.e., one containing distilled water (“test compartment”) and the other containing 3% NaCl solution was designed. The cylindrical mortar specimen was placed in between the two compartments. To study the inhibitor effect, critical period of corrosion initiation, and threshold chloride concentration, the electrochemical tests such as open circuit potential, and electrochemical impedance spectroscopy measurements were carried out on the steel specimens having diameter of 6 mm and exposed surface area of 0.28 cm^2 at regular intervals up to 180 days. The electrochemical measurements were carried out on the steel specimen in the “test compartment” of the diffusion cell. In addition, the chloride concentration of solution in the “test compartment” was measured periodically using a chloride specific electrode ORION 96-17 at regular intervals up to 180 days. The chloride concentration was used to estimate the apparent chloride diffusion coefficient using Fick’s first law of diffusion. Further, the microstructure of mortar was studied by scanning electron microscope combined with energy dispersive X-ray spectroscopy analysis. Based on the obtained results, the authors reported that the presence of phosphates in mortar increased the critical period of pitting corrosion initiation from 30 to 100 days and significantly decreased the rate of chloride diffusion. The microstructure analysis confirmed that the addition of Na_3PO_4 resulted in the formation of phosphate compounds that blocked the pores, and effectively reduced the chloride diffusion in mortar.

Xing et al. [132] have studied the influence of chloride ion on the content and distribution of free NO_2^- ion in the cement paste exposed to chloride solution using chemical quantitative analysis method. For this purpose, cement paste specimens of size $40 \text{ mm} \times 40 \text{ mm} \times 160 \text{ mm}$ were prepared using Type I ordinary Portland 42.5 cement at w/c of 0.30, 0.40, and 0.50. Sodium nitrite as corrosion inhibitor was added at the NO_2^- concentrations

of 0.5%, 1%, 1.5%, and 2% by weight of cement during the preparation of cement paste. After 28 days of curing, the surfaces of the cement paste specimens were coated with epoxy resin leaving only one surface uncoated for one-dimensional diffusion of chloride ions. The paste specimens were divided into two groups representing different exposure conditions. The first group was exposed to 2% chloride solution prepared from NaCl, whereas the second group was soaked in aqueous solution. After 7 days of exposure, the specimens were sliced at 10 mm intervals and ground into powder samples. The free NO_2^- ion of cement paste samples was measured by spectrophotometric method. In addition, X-ray diffraction (XRD) and scanning electron microscope (SEM) analyses were also carried out on the cement paste samples. Based on the obtained results, the authors observed that in case of cement paste exposed to chloride solution, the amount of free NO_2^- ion was more as compared to that exposed to aqueous solution due to the competitive adsorption of chloride ions with NO_2^- ions on the surface of C-S-H and the chemical substitution of chloride ion for NO_2^- -AFm. In the cement paste exposed to chloride solution, the free NO_2^- ion concentration was lowest on the surface of erosion, and highest at 10 mm from the erosion surface. The XRD and SEM analyses showed the formation of NO_2^- -AFm in the cement paste containing sodium nitrite.

Chen et al. [133] have studied the impact of three phosphate based corrosion inhibitors on chloride binding and chloride release in cement pastes through chloride binding isotherms i.e., Langmuir chloride binding isotherm and Freundlich chloride binding isotherm, X-ray diffraction (XRD) analysis, and thermogravimetric analysis (TGA). For this purpose, cement paste specimens of size 40 mm × 40 mm × 160 mm were prepared using ordinary Portland cement (OPC) with two w/c such as 0.40 and 0.50. The phosphate based corrosion inhibitors used were sodium monofluorophosphate (MFP), di-Sodium hydrogen phosphate (DHP), and trisodium phosphate (TSP). The corrosion inhibitors were applied to the cement pastes in two ways: as admixture phosphate and as migrating phosphate. In case of admixture phosphate, the corrosion inhibitors were added to the mixing water at the concentration of 1%, 3%, and 5% each by weight of cement during the preparation of cement paste. The prepared specimens were cured for 84 days under 95% relative humidity condition. In case of migrating phosphate, the cement paste specimens were prepared without the corrosion inhibitors. After 28 days of curing (95% relative humidity condition), the prepared specimens were immersed in phosphate aqueous solutions (concentrations of 0.1, 0.2, and 0.3 M) for another 56 days. In addition, another group of cement paste

specimens was prepared using w/c of 0.5 and admixed with NaCl at the concentration of 0.5%, 1%, 2%, 3%, and 5% by weight of cement. After curing and exposure, all the cement paste specimens were crushed and powder samples were collected. The powder samples were used to determine the chloride binding, chloride release in deionized water, and chloride release in phosphate solution through potentiometric titration. For chloride binding test, the powder samples (obtained from admixture phosphate, and migrating phosphate paste specimens) were mixed with different concentrations of NaCl solution (0.01, 0.05, 0.1, 0.3, 0.5, 1.0, and 1.5 mol/l) and kept for a period of 2 months to establish the equilibrium condition. For determination of chloride release in deionized water, the powder samples used for chloride binding were filtered thoroughly, and then mixed with deionized water and subsequently kept for 2 months to establish the equilibrium condition. In case of chloride release in phosphate solution test, the powder samples (obtained from NaCl admixed paste specimens) were immersed in deionized water, MFP or TSP solutions (0.2 M), and DHP solutions (0.1, 0.2, and 0.3 M) for two weeks. In addition, the mass fractions of solid phases in cement paste samples were also determined by using XRD, TGA, and reference intensity ratio (RIR) analyses. From the obtained results, the authors reported that the use of phosphate based inhibitors (as admixture phosphate or as migrating phosphate) decreased the chloride binding capacity of cement paste as compared to that admixed with only chloride. In terms of decreasing chloride binding capacity, the trend for the three types of phosphates was TSP > DHP > MFP. The XRD analysis indicated that the increase in dosage of phosphate led to an increase in the diffraction peak areas of apatite and bearthite, and decrease in the diffraction peak areas of Friedel's salt. The authors concluded that the release of bound chloride could be well calculated by chloride binding isotherms. The modified chloride binding isotherms were established that correlated bound chloride contents with effective phosphate concentration.

2.3.2 Review of literature on effect of corrosion inhibitors in both cementitious composites and simulated concrete pore solution

Andrade et al. [103] have investigated the use of $\text{Na}_2\text{PO}_3\text{F}$ (MFP) as a curative corrosion inhibitor for steel reinforcement in mortar. For this purpose, the effectiveness of $\text{Na}_2\text{PO}_3\text{F}$ against steel reinforcement corrosion was evaluated in chloride contaminated saturated $\text{Ca}(\text{OH})_2$ solution as well as in chloride contaminated mortar by using half-cell potential and linear polarization resistance measurements. The test solution was prepared by adding NaCl (0.5 M) and different concentrations of $\text{Na}_2\text{PO}_3\text{F}$ (0, 0.05, 0.1, and 0.5 M) in saturated

Ca(OH)₂ solution. The corrosion of steel bar (with an exposure area of 6 cm²) exposed to chloride contaminated saturated Ca(OH)₂ solution for 35 days was monitored through pitting potential (from potentiodynamic polarization test), corrosion potential, and corrosion current density. Three groups of mortar specimens of size 80 mm × 55 mm × 20 mm were made using ordinary Portland cement at water-to-cement ratio of 0.5 and cement-to-sand ratio of 1:3. Two steel bars (exposure area of 6 cm² each), and one graphite bar as auxiliary electrode were embedded in each mortar specimen. The first group of mortar specimens was made by admixing NaCl (0.5 M) and Na₂PO₃F (0, 0.05, 0.1, and 0.5 M) during the preparation of mortar and subjected to wetting and drying cycles (50% and 100% relative humidity). The second group of mortar specimens was prepared without any admixture. After curing, NaCl and Na₂PO₃F were applied on the surface of the specimens for an exposure period of 55 days. The third group of mortar specimens was prepared with or without admixed NaCl (0.5 M). The specimens were cured for 7 days and then subjected to wetting-drying cycles (5 hours immersion, and 4 days drying) in 0.5M NaCl plus (0.1 M or 0.5M) Na₂PO₃F solution (in case of mortar without admixed NaCl), and in (0.1 M or 0.5 M) Na₂PO₃F solution (in case of mortar with admixed NaCl). From the obtained results, the authors observed that in the presence of chloride, Na₂PO₃F was more effective in mortar than in test solution (simulated pore solution) for the same inhibitor concentration. The steel reinforcement in mortar specimens showed 10 times lower corrosion current density as compared to that in the test solution. The authors also observed that for efficient inhibition effect, the minimum ratio of [MFP⁻]/[Cl⁻] is 1.

Saricimen et al. [88] have carried out an experimental investigation to evaluate the effectiveness of two corrosion inhibitors in retarding rebar corrosion in concrete as well in saturated Ca(OH)₂ solution. For concrete test, the authors have prepared reinforced concrete specimens of size 100 mm × 65 mm × 300 mm with a centrally placed 12 mm diameter steel bar using ASTM C150 Type-V cement. Two concrete mixes, one admixed with corrosion inhibitor and the second one admixed with corrosion inhibitor and NaCl (1.5% by weight of cement) were prepared. A proprietary alkanolamine inhibitor (M2) at the dosage of 5 l/m³ of concrete and a water-based inorganic inhibitor (R2) at the dosage of 1.2 kg/m³ of concrete were admixed during the preparation of concrete. After curing, the reinforced concrete specimens were exposed to 5% NaCl solution. The authors have performed accelerated corrosion test (for two months or until cracking of the specimens), linear polarization resistance (LPR) measurements (before and after completion of

accelerated corrosion test), and AC impedance spectroscopy (before cracking and after cracking) on the specimens made from the concrete mix admixed with only corrosion inhibitors. Corrosion of the specimens prepared from the second mix (admixed with corrosion inhibitors and NaCl) was monitored regularly by linear polarization resistance (LPR) measurement. In addition, anodic polarization measurement was performed on the steel specimens (size: 10 mm diameter and 2 mm thick) exposed to saturated Ca(OH)_2 solution containing NaCl and corrosion inhibitors for 48 and 96 hours. The surface of steel specimen was also analyzed using electron spectroscopy for chemical analysis (ESCA) and auger electron spectroscopy (AES) to understand the inhibition mechanism of the inhibitors in the presence of chloride ions. The results obtained from different tests indicated that in both concrete and saturated Ca(OH)_2 solution, inorganic inhibitor R2 was more effective than organic inhibitor M2 in retarding rebar corrosion. The authors have observed that in case of specimens admixed with R2 corrosion inhibitor, the corrosion rate was less, corrosion potential was more positive, and time to initiation of corrosion was more as compared to that admixed with M2 corrosion inhibitor. The surface analysis indicated that both the corrosion inhibitor modified the passive film over the steel surface and protected the steel against corrosion. The presence of organic oxygen and chlorine in the composition of M2 corrosion inhibitor may be the reason behind its inferior performance as compared to R2 corrosion inhibitor.

Dhouibi et al. [105] have carried out a study to assess the efficiency of sodium phosphate and sodium nitrite as corrosion inhibitors against steel reinforcement corrosion in both simulated concrete pore solution and concrete. For solution test, chloride-contaminated concrete pore solution (pH 11.6) was prepared using saturated calcium hydroxide with 0.5 M sodium chloride. Different concentrations of sodium phosphate and sodium nitrite were added to the concrete pore solution. The authors have performed electrochemical impedance spectroscopy (EIS), polarisation curve (PC), and open circuit potential measurements (OCP) using three-electrode cell containing a carbon steel (33 mm² area) as working electrode, saturated calomel electrode as reference electrode, and a platinum wire as the counter electrode. For concrete test, prismatic specimens of size 40 mm × 40 mm × 160 mm with a steel reinforcement of 6.5 mm diameter were prepared using ordinary Portland cement, sand, and gravel with a w/c of 0.40. Corrosion inhibitors were added at the dosage of 6% by weight of cement during the preparation of concrete mixes. After 28 days of curing, the specimens were immersed either in distilled water (as reference

condition) or in 0.5 M NaCl solution for three years, and EIS and OCP tests were carried out once a year during this period. After 3 years of exposure, concrete near the steel was analyzed by X-ray diffraction (XRD) analysis, Fourier infrared spectroscopy (FT-IR) analysis, scanning electronic microscopy (SEM) analysis, energy dispersion spectroscopy (EDS) analysis, and chloride content measurement. From the results of electrochemical tests in solution, the authors observed that phosphate prevented pitting corrosion when its content was equal to chloride concentration, and nitrite contributes only to the increase in value of pitting potential. The addition of corrosion inhibitors reduced the corrosion rate of steel reinforcement in the simulated concrete pore solution. In concrete, the obtained results indicated that after 1 year of immersion in aggressive environment, the corrosion rate decreased in the presence of corrosion inhibitors. However, after 3 years of immersion, no influence of inhibitors on the corrosion rate was observed. After 3 years of exposure, visual examination of specimens showed that all steel bars were corroded in the presence of chlorides. In the presence of corrosion inhibitors, the free chloride content at the rebar level was lower as compared to the concrete without inhibitors, however, its value was higher than the critical chloride threshold value. After three years of exposure, the microstructure analysis showed possible wash out of nitrites from concrete during immersion in chloride solution.

Ormellese et al. [90] have investigated the effectiveness of three organic corrosion inhibitors such as amine-esters (C), aminoalcohols (D), and alkanolamines (E) and one nitrite based inhibitor i.e., calcium nitrite against chloride induced steel reinforcement corrosion in Ca(OH)_2 solution as well as in concrete. For solution test, the corrosion inhibitors i.e., C, D, E, and N were added in Ca(OH)_2 solution at the dosage of 30 g/l, 60 g/l, 10 g/l, and 50 g/l respectively. Carbon steel bars of 16 mm diameter with an exposure area of 200 mm² were used as test specimens for potentiodynamic and potentiostatic tests in saturated Ca(OH)_2 solution. Prior to the tests, the steel specimens were immersed for 48 h in Ca(OH)_2 solution containing corrosion inhibitor for passivation. After that, 0.2% chloride was added in Ca(OH)_2 solution at every 48 h, till chloride percentage reached up to 3%. For concrete test, the authors have prepared two concrete mixes i.e., Mix 1 with cement content of 300 kg/m³, and Mix 2 with cement content of 400 kg/m³ using CEM II A/L 42,5R cement at w/c of 0.50. From the concrete mixes, three series of concrete specimens of size 250 mm × 160 mm × 70 mm were prepared. The first series was prepared from Mix 1 admixed with chloride (1% and 1.5% by weight of cement) and corrosion

inhibitors (at the suggested dosage by the manufacturer). The second series was prepared from Mix 2 and admixed with chloride (1% and 1.5% by weight of cement) and corrosion inhibitors (at the maximum allowed dosage). The third series was prepared from Mix 1 admixed with only corrosion inhibitors (at the suggested dosage by the manufacturer). The third series of specimens were subjected to ponding cycles consisting of 1 week wetting in 3.5% NaCl solution followed by 2 weeks drying to accelerate the corrosion process. A carbon steel rebar of 10 mm diameter and 270 mm length, two stainless steel rebars of diameter 10 mm, and a stainless wire were placed in concrete specimen for corrosion potential and linear polarization resistance (LPR) measurements. At the end of electrochemical test, visual inspection and weight loss measurements were carried out on the steel rebar. The authors have also analyzed the total chloride content of the specimen prepared from series 3 by potentiometric titration. From the results, the authors observed that in simulated pore solution, the inhibitors D and E showed very poor effect against corrosion as they are volatile amines, whereas inhibitor C showed effective inhibition properties both at low and high chloride concentrations. In concrete, all the four inhibitors were able to delay the occurrence of chloride induced corrosion, and the organic inhibitors reduced the ingress of chloride ion by filling and blocking the concrete pores by the formation of complex compounds. There was no clear and significant effect of organic inhibitors on the corrosion rate of rebar in concrete.

Etteyeb et al. [134] have investigated the efficiency of sodium phosphate pretreatments applied on steel rebar against chloride induced steel reinforcement corrosion in synthetic concrete pore solution and mortar. For solution test, saturated $\text{Ca}(\text{OH})_2$ solutions (pH of 12.6) admixed with NaCl at different concentrations (i.e., 0, 0.1, 0.3 and 0.5 M chloride ion) were used as synthetic concrete pore solution. The electrochemical behavior of steel specimen (size 6 mm in diameter and 30 mm in length) in synthetic concrete pore solution was assessed through corrosion potential, polarization resistance, and electrochemical impedance spectroscopy measurements. Prior to the electrochemical measurements, the steel specimens were prepassivated for 24 hours in 0.5 M Na_3PO_4 solution. For mortar test, prismatic mortar specimens of size 80 mm $\times$ 55 mm $\times$ 20 mm were prepared using ordinary Portland cement at water-to-cement ratio (w/c) of 0.50 and cement to sand ratio (c/s) of 1:3. The mortar specimens were prepared with and without admixed chloride (1% NaCl by weight of cement). Two steel bars (as working electrode) and a graphite bar (as auxiliary electrode) were embedded into each mortar specimen during preparation. Corrosion

potential and polarization resistance measurements were performed on the mortar specimens. Before embedding into the mortar specimens, some of the steel bars were prepassivated for 24 hours in 0.5 M Na_3PO_4 solution. The reinforced mortar specimens prepared without admixed NaCl were subjected to 33 wetting-drying cycles. One wetting-drying cycle comprised of 1 day of wetting in 0.5 M NaCl solution followed by 2 days of drying. Based on the obtained results from the electrochemical measurements, the authors reported that in synthetic concrete pore solution, pretreatment of steel rebar using phosphate favoured the formation of a passive layer over the steel reinforcement and increased the resistance to corrosion initiation up to the chloride concentration of 0.3 M. However, at chloride concentration of 0.5 M in synthetic concrete pore solution, insufficient inhibiting action of Na_3PO_4 against steel reinforcement corrosion was observed. Further, the steel rebar in mortar exposed to chloride solution remained passive for a longer period as compared to the steel rebar in chloride admixed mortar. The authors concluded that in all cases of mortar, the effect of phosphate treatment against corrosion of steel reinforcement was temporary.

2.4 Effect of cation type associated with chloride ions on chloride ingress, chloride binding, and steel reinforcement corrosion in cementitious composites

In this section, the research work carried out by different researchers on the effect of cation type associated with chloride ions on chloride ingress, binding of chloride ions, corrosion of steel reinforcement, and microstructure of cementitious composites exposed to chloride and composite chloride-sulfate environment are presented and discussed.

Hansson et al. [54] have studied the effect of cations i.e., K^+ , Na^+ , and Ca^{2+} associated with chloride ions on corrosion rate of steel in mortar. For this purpose, mortar prism specimens of size 40 mm $\times$ 40 mm $\times$ 160 mm with a centrally embedded steel bar were prepared using ordinary Portland cement (OPC) at cement: sand: water proportion of 1: 3: 0.50. Three chloride salts namely, KCl, NaCl, and CaCl_2 were added to the mixing water at different chloride concentrations (i.e., 0, 0.5, 1.0, and 2.0% of Cl^- by weight of cement) during the preparation of mortar mixes. The mortar specimens were demoulded after 4 days of preparation and then exposed to 0.5% chloride solution of the corresponding chloride salts for 60 days. The polarization resistance of steel in mortar specimens was measured to determine the corrosion rate. Further, total porosity, pore size distribution by mercury porosimetry, and relative electrical resistances of mortar specimens were also determined. In addition, to analyze the pore solution of mortar, specimens of size 50 mm in diameter

and 50 mm in length were prepared using the same mortar mixes as prepared for the electrochemical measurement. The pore solution was expressed from the mortar samples by the application of pressure. The concentrations of K^+ , Na^+ , and Ca^{2+} in the extracted pore solution of mortar were determined using flame photometry and the concentrations of $(OH)^-$ and Cl^- were determined using titration techniques. Based on the obtained results, the authors reported that $CaCl_2$ was more aggressive than $NaCl$ or KCl as the corrosion rates were 2 to 4 times higher for $CaCl_2$ than other two chloride salts. The amount of dissolved chloride ion in mortar pore solution was in the decreasing order of $Na^+ > K^+ > Ca^{2+}$. In OPC mortar, the addition of $CaCl_2$ produced more open pore structure that allowed easier diffusion of aggressive ions, and increased the electrical conductivity thereby resulting in higher corrosion rate as compared to KCl and $NaCl$. In addition, the addition of $CaCl_2$ lowered the pH of pore solution than KCl and $NaCl$. The authors concluded that the total chloride content or the dissolved chloride content in the pore solution alone can not be used as a measure of corrosion rate. For initiation of steel corrosion, a certain minimum chloride content may be necessary, but the subsequent rate of corrosion is controlled by other factors such as resistivity, porosity, pH, and availability of oxygen.

Arya et al. [135] have carried out an investigation to study the effect of different factors such as cement type, supplementary cementitious materials, water-to-cement ratio (w/c), hydration time, curing temperature, percentage of chloride ions, and associated cation type on chloride binding in cement paste. Cement pastes were prepared using normal ordinary Portland cement (OPC1), high alkali OPC (OPC2), sulfate resisting Portland cement (SRPC), and OPC replaced with pulverized fuel ash (PFA, replacement levels of 15% and 35%), ground granulated blast furnace slag (GGBS, replacement level of 70%), and silica fume (SF, replacement level of 15%) at three w/c of 0.40, 0.50, and 0.60. The experimental study was divided into two phases i.e., Phase I: for internal chloride, and Phase II: for external chloride. For Phase I, $NaCl$ and $CaCl_2$ (each at concentrations of 0.5, 1, and 2% Cl by weight of cement) were added during the preparation of cement paste. Cylindrical paste specimens of size 45 mm diameter and 58 mm height were prepared and cured at different curing temperatures for different periods. For Phase II, cylindrical paste specimens of size 49 mm diameter and 10 mm height were prepared without admixed chloride salts. After 24 hours of preparation, the paste specimens (prepared for Phase II) were cut into $6\text{ mm} \pm 0.5\text{ mm}$ discs, and exposed to various concentrations of chloride salt solutions i.e., $NaCl$ at 20 g/l, 45g/l, and 90g/l; $MgCl_2$ at 20g/l, and $CaCl_2$ at 20g/l, and sea water for different exposure

periods. At the end of curing, the pore press method was used to extract the pore solution of cement paste specimens prepared for both Phase I and Phase II. The obtained pore solution was then used to determine the chloride ion content of cement paste using potentiometric titration. From the obtained results, the authors have observed that for internal chloride condition (Phase I), cement type, proportion and type of cement replacement materials, associated cation type, and total chloride content were the most important factors for chloride binding. In case of Phase I, the chloride binding increased with an increase in w/c, curing temperature, and age. Further, the use of OPC with higher alkali content or use of PFA replacement or GGBS replacement increased the chloride binding while the chloride binding decreased in case of SF replacement and SRPC cement. For external chloride condition (Phase II), the effect of OPC and cement replacement materials on chloride binding was similar to that observed in case of Phase I, however, the differences in chloride binding capacity between different binders were less pronounced in case of external exposure. The authors reported that the C_3A content had little effect on chloride binding as OPC and SRPC showed similar chloride binding behavior. Further, in case of external chloride condition, the w/c and curing time showed little effect on chloride binding. However, the chloride binding increased with exposure time, and chloride concentration. Further, the specimens exposed to $MgCl_2$ solution showed higher chloride binding than $CaCl_2$ solution followed by $NaCl$ solution.

Dehwah et al. [136] have experimentally investigated the effect of sulfate concentration and associated cation type on chloride-induced reinforcement corrosion in concrete exposed to chloride and mixed chloride-sulfate solutions for a period of 1200 days. Reinforced concrete specimens (of size 75 mm diameter and 150 mm height) with a centrally embedded 12 mm diameter steel bar were prepared using two ordinary Portland cements (having C_3A contents of 8.5%, and 9.65%) and sulfate resisting Portland cement (C_3A content: 3.6%) at a w/c of 0.45. After 28 days of curing, the concrete specimens were kept at room temperature for one week and then partially immersed in chloride and mixed chloride-sulfate exposure solutions. For chloride exposure, 5% $NaCl$ solution was used. For mixed chloride-sulfate exposure, mixed solution of 5% $NaCl$ and sodium sulfate (1%, 2.5%, and 4% SO_4^{2-}) or magnesium sulfate (1%, 2.5%, and 4% SO_4^{2-}) were used. The corrosion of steel in reinforced concrete specimens was monitored through corrosion potential and corrosion current density. From the obtained results, the authors have observed that the presence of sulfate ions did not influence the time-to-initiation of steel

reinforcement corrosion but the corrosion rate increased with increase in sulfate ion concentration. Further, the time-to-initiation of steel reinforcement corrosion was more in ordinary Portland cement concrete as compared to sulfate resisting Portland cement concrete. The corrosion rate was more in case of exposure to composite chloride-sulfate solutions as compared to exposure to only chloride solution. The authors reported that the corrosion rate in concrete exposed to sodium chloride plus magnesium sulfate solutions was higher than that exposed to sodium chloride plus sodium sulfate solutions. Further, the corrosion rate of steel reinforcement decreased with increase in C_3A content in the cement.

Poursaee et al. [137] have studied the effect of $NaCl$, $MgCl_2$, and $CaCl_2$ salts on macro-cell corrosion and micro-cell corrosion of steel bars in ordinary Portland cement mortar. Mortar mixes were prepared using Type 10 Portland cement at water: cement: sand proportion of 0.5: 1: 3. In this study, mortar prisms of size 152 mm $\times$ 152 mm $\times$ 102 mm and embedded with four steel reinforcing bars of 6.35 mm in diameter and 228.6 mm in length were prepared. In the mortar prisms, one bar was positioned at the top with a cover depth of 9.7 mm and three bars at the bottom with the same cover depth. The vertical surfaces of the mortar prisms were coated with epoxy resin to prevent access of oxygen. At the top surface of the specimens, a well was attached for ponding of exposure solutions. The specimens were subjected to wetting drying cycles for 124 weeks with one cycle consisting of 2 weeks of wetting in 3% chloride solution prepared from $NaCl$, $MgCl_2$, and $CaCl_2$ followed by 2 weeks of drying. After 124 weeks, the concentration of chloride ions in the exposure solutions was changed to 30% and the exposure was continued for another six weeks. The macro-cell corrosion and micro-cell corrosion of steel bars were monitored by linear polarization resistance (LPR) measurement. In addition, XRD analysis was performed on cement powders obtained from the mortar specimens. From the obtained results, the authors observed that at 3% chloride concentration, the specimens exposed to $CaCl_2$ and $NaCl$ solutions exhibited higher micro-cell corrosion current density than those exposed to $MgCl_2$ solution. The macro-cell corrosion current density indicated that for the first 70 weeks of exposure at 3% chloride concentration, the corrosion was active only in the specimens exposed to $CaCl_2$ solution. At 30% chloride concentration, the deterioration of steel in mortar specimens was severe in case of exposure to $CaCl_2$ solution, lesser extent for exposure to $MgCl_2$ solution, and no corrosion damage in case of exposure to $NaCl$ solution. The results of XRD analysis indicated the presence of hydrated calcium monochloroaluminate in the mortar exposed to $CaCl_2$ solution.

Dousti et al. [23] have carried out an investigation to study the effect of w/c, silica fume replacement, and chloride concentration on chloride binding of concrete exposed to sea water in the Persian Gulf region. For this purpose, four series of concrete mixes were prepared using Portland cement (ASTM Type II) and silica fume at the water-to-cementitious material ratios (w/cm) of 0.35, 0.40, 0.45, and 0.50. The cement was replaced with silica fume by 5%, 7.5%, 10%, and 12.5% by weight of cement. Concrete prisms of size 150 mm × 150 mm × 600 mm were made and cured in saturated calcium hydroxide solution for 28 days. After curing, the specimens were sealed on four sides using epoxy coating in order to ensure one dimensional diffusion of chloride ions. The prismatic specimens were then subjected to tidal zone exposure condition on the shore of Persian Gulf region for 5 years. After completion of exposure, concrete section of size 150 mm × 150 mm × 100 mm was cut from the prismatic specimens. Powder samples obtained from different depth intervals of the concrete section was used for the determination of free chloride and total chloride content of concrete. Based on the obtained results, the authors reported that with increase in w/cm, the amount of bound chloride of concrete increased. Further, the total chloride and bound chloride contents decreased with an increase in silica fume replacement level in concrete. The authors also reported that with an increase in chloride concentration in the concrete pore solution, the bound chloride of concrete increased. The authors concluded that for various types of concrete mixes in field condition (for total chloride concentration less than 1.2% by weight of concrete), the relationship between bound and total chloride contents is generally linear.

Xu et al. [138] have investigated the influence of CaCl_2 and NaCl from internal and external sources on chloride threshold value for corrosion of steel reinforcement in concrete. Concrete cube specimens of size 100 mm and embedded with a steel bar of 10 mm diameter and 60 mm length were prepared using 42.5 ordinary Portland cement at w/c of 0.55. For internal chloride exposure, seven levels of NaCl and CaCl_2 ranging from 0.1% to 2% by mass of cement were added in the concrete mixes during preparation. After demoulding the specimens were cured for 3 months in a 95% humidity chamber and then immersed in $\text{Ca}(\text{OH})_2$ solution for 8 hours before testing. In case of external chloride exposure, cube specimens (without admixed chloride) were cured for 28 days. After completion of curing, the surfaces of the cubes were coated with paraffin wax leaving one surface parallel to the steel bar uncoated to facilitate one directional ingress of chloride ions. Thereafter, the specimens were subjected to wetting-drying cycles with one cycle

consisting of 3 days of wetting in 0.50 mol/l NaCl or 0.25 mol/l CaCl₂ solutions followed by drying for 4 days. Corrosion of steel in cube specimens was measured through electrochemical techniques such as half-cell potential and linear polarization measurements till active corrosion was confirmed. For both internal and external chloride exposure, pH, free chloride content, and total chloride content of cement paste adjacent to the steel reinforcement in concrete were measured after completion of corrosion tests. Besides, the acid neutralization capacity and release of bound chloride of cement paste obtained from the specimens admixed with 1.5% NaCl (by mass of cement) were also measured. Langmuir isotherm and Freundlich isotherm were used to describe the nonlinear chloride binding of concrete containing internal NaCl, and CaCl₂. From the obtained test results, the authors reported that in case of internal exposure, with an increase in NaCl concentration, the pH value first increased and then decreased, whereas for CaCl₂, the pH value decreased with increase in concentration of CaCl₂. Further, the amount of bound chloride was more in the concrete exposed to internal CaCl₂ than that exposed to internal NaCl. For both internal and external exposure, the specimens containing CaCl₂ showed more negative half-cell potential value and higher corrosion rate than the specimens containing NaCl. The ranges of chloride threshold values for the corrosion expressed as free chloride ion, total chloride ion, and $[Cl^-]/[OH^-]$ ratio were higher for the specimens with internal NaCl as compared to that with internal CaCl₂. However, the chloride threshold values for the corrosion expressed as free chloride ion and $[Cl^-]/[OH^-]$ ratio were lower for the specimens exposed to external NaCl solution than those exposed to external CaCl₂ solution.

Zhu et al. [52] have carried out a study to evaluate the effect of different cations of chloride i.e., Na⁺, K⁺, Mg²⁺, and Ca²⁺ on the binding mechanism of chloride ions in concrete through chloride ions concentrations test, pH measurement, XRD, and TG-DTG techniques. Concrete cube specimens of size 100 mm were prepared using OPC, 20 mm MSA crushed aggregate, sand, and water reducing admixture. Steel sticks were inserted in the concrete with a cover depth of 15 mm during preparation. The authors have used three w/b such as 0.35, 0.42, and 0.49 for the preparation of concrete mixes. The specimens were cured for 28 days and were then dried for 4 days. After that, the specimens were subjected to 7-day wetting-drying cycles, which included immersion of the specimens for 4 days in 10% chloride salt solution prepared from NaCl, KCl, MgCl₂ and CaCl₂ followed by 3 days drying at room temperature. The specimens were subjected to 24 wetting-drying cycles. The specimens were then tested for free and total chloride concentrations through

potentiometric titration, and pH value was also measured. The authors have also carried out XRD analysis and TG-DTG analysis on the slurry powder collected from the depth of 2 mm within the surface of steel specimen. From the results, the authors concluded that chloride binding capability and the pH of pore solution are greatly affected by the cation type associated with chloride ions. The free chloride content and bound chloride content of concrete with cation type were in the order: C_f : $\text{Na}^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$, and C_b : $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ \approx \text{K}^+$. The sodium cation (Na^+) increased the pH of concrete pore solution, which increased the solubility of Friedel's salt to release the bound chlorides. The magnesium cation (Mg^{2+}) decreased the pH as a result of reaction with C–S–H, and showed less free chloride ions than Na^+ and K^+ .

Jiang et al. [55] have carried out an experimental investigation to evaluate the influence of chloride salt type on corrosion of steel reinforcement in chloride contaminated simulated concrete pore solution considering chloride threshold level as an essential parameter for corrosion. The authors have prepared two types of simulated concrete pore solution, i.e., saturated $\text{Ca}(\text{OH})_2$ solution and OPC cement extract. Chloride salts such as KCl, NaCl, CaCl_2 , and MgCl_2 were used as the sources of chloride ions. The chloride salts were added stepwise each day to the test solutions at the dosage of 0.01 mol/l (concentration of Cl^- ions). The initiation of pitting corrosion of steel reinforcement exposed to chloride contaminated simulated concrete pore solutions was determined by open-circuit potential (E_{corr}) measurement and electrochemical impedance spectroscopy (EIS) measurement. Steel specimens of size 10 mm diameter and 30 mm length were used as test specimens in the electrochemical measurements. Prior to the electrochemical measurements, the steel specimens were immersed in the test solutions (without admixed chloride ions) for 7 days to promote the passivation of steel. After 7 days of immersion, the initial open-circuit potential (E_{corr}) value was measured and after that, the E_{corr} values were recorded at 1-day interval, immediately before adding the new chloride dose. The pH value of the test solutions was also determined periodically. From the obtained results, the authors observed that the addition of NaCl and KCl had negligible effect on the pH of saturated $\text{Ca}(\text{OH})_2$ solution, whereas in cement extract they initially increased and then decreased the pH value. The additions of MgCl_2 and CaCl_2 significantly reduced the pH values of both saturated $\text{Ca}(\text{OH})_2$ solution and cement extract. It was also observed that with increase in dosages of NaCl, KCl, MgCl_2 , and CaCl_2 additions, the open-circuit potential (E_{corr}) of steel became more negative, and the corrosion current density (determined from EIS

measurement) increased. The addition of chloride salts had a significant influence on the threshold level for the corrosion of steel reinforcement, and chloride salts with the same valent cation such as NaCl, KCl, and MgCl_2 , CaCl_2 resulted in identical threshold levels in both test solutions.

Weerdt et al. [139] have studied the influence of magnesium and sulfate present in seawater on chloride binding in Portland cement paste. For this purpose, cement paste was prepared using CEM I 42.5 Portland cement at w/c of 0.40. The prepared cement paste was cured for 7 days in the water bath and then ground to 1 mm fine particles. After that, the cement powders were cured in 40% of water by mass of powder for another 7 days. Thereafter, the moist hardened cement paste was further crushed and stored in air tight polypropylene bottles until analysis of the sample. TGA was carried out to determine the free water present and degree of hydration of wet paste. Further, the cement paste samples were exposed to different chloride and composite chloride-sulfate solutions prepared from NaCl, MgCl_2 , NaCl+ MgCl_2 , MgCl_2 + MgSO_4 , and sea water ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NaCl, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, and KCl) for 2 months. The cement paste powder samples were studied by carrying out pH measurement, and potentiometric titration for chloride content. The free chloride content was calculated from the chloride concentration of the added exposure solution, and bound chloride was determined from the measured equilibrium chloride content in the liquid phase. The chloride contents were used for the determination of chloride binding isotherms. In addition, microstructure studies using SEM-EDS analysis were carried out on the selected cement paste samples. From the obtained results, the authors observed that the chloride binding in Portland cement paste exposed to sea water was similar to that exposed to NaCl, NaCl+ MgCl_2 , and MgCl_2 + MgSO_4 solutions for all chloride concentrations. The chloride binding was higher in the specimens exposed to MgCl_2 solution as compared to other chloride-containing solutions, which was caused by the decrease in pH of cement paste in the presence of MgCl_2 . Further, the magnesium content in the sea water resulted in a slight decrease in pH, however, this did not result in a notable increase in chloride binding. The presence of sulfate in sea water decreased the chloride binding in cement paste due to the conversion of a part of the AFm phases into ettringite.

Song et al. [37] have experimentally investigated the effect of four cation types i.e., K^+ , Na^+ , Ca^{2+} , and Mg^{2+} on chloride binding, and diffusion behavior of chloride ions in concrete exposed to chloride salt solutions. Concrete slab specimens of size 2000 mm $\times$ 2000 mm $\times$

200 mm were prepared using Type II Portland cement at w/c of 0.50. The slab specimens were cured for 90 days and then, cylindrical specimens of 100 mm in diameter and 50 mm in height were drilled out from them. The side and bottom surfaces of the cylindrical specimens were sealed with epoxy coating while the top surface was exposed to aqueous solutions prepared from different chloride salts for a period of 180 days. The chloride salts used for the preparation of aqueous solution were NaCl (0.5 mol/l), KCl (0.5 mol/l), CaCl₂ (0.25 mol/l), and MgCl₂ (0.25 mol/l). After the end of exposure, concrete powder samples were collected layer by layer and used to determine the water-soluble chloride and total chloride contents. X-ray diffraction (XRD) analysis was performed on the powder samples collected from the depth of 1-3 mm from the exposure surface of the cylindrical specimens. The Fick's 2nd law of diffusion was used to determine the apparent diffusion coefficient. In addition, numerical simulations considering multi-phase reactions and ionic interactions were conducted to improve an existing mathematic model to study the influence of cation type on chloride diffusion behavior in concrete. From the obtained results, it was observed that the cation associated with chloride ions influenced the diffusion of chloride ions into concrete, which was mainly due to the difference in chloride binding capacity. The chloride binding capacity with the cation type decreased in the order of Ca²⁺ > Mg²⁺ > Na⁺ ≈ K⁺. The chloride ions associated with monovalent cations, i.e., K⁺, and Na⁺ had higher apparent diffusion coefficient as compared to those associated with divalent cations, i.e., Ca²⁺ and Mg²⁺ and the apparent diffusion coefficient of chloride ions with cation type decreased in the order of K⁺ ≈ Na⁺ > Ca²⁺ > Mg²⁺. The XRD analysis showed that CaCl₂ increased the formation of Friedel's salt and decreased the leaching velocity of Ca(OH)₂. From the improved chloride diffusion model, the authors reported that the chloride binding capacity of concrete in natural diffusion process is a complicated function concerning many factors. Among the factors, the cation type associated with chloride ions, and the contact duration between chloride ions and cement hydrates are significantly important.

Geng et al. [47] have studied the effect of sulfate attack on stability of bound chlorides in chloride contaminated cement paste containing fly ash and GGBS. Cement paste was prepared using Type 42.5 ordinary Portland cement (OPC), grade II fly ash, and GGBS at w/b of 0.50. The cement was replaced with fly ash and GGBS (for both single and combined replacement) at the replacement level of 30% by weight of binder. In case of combined replacement, fly ash and GGBS were used in the proportions of either 1:1 or 7:3. For chloride contamination in cement paste, NaCl at the concentration of 0.5 mol/l was added

with mixing water during preparation. Three groups of paste specimens (size: 40 mm × 40 mm × 160 mm) were prepared for different exposure conditions. The first group was cured in standard curing condition for 1, 3, 7, 14, 28, 56, and, 90 days to study the effect of curing time as well as fly ash and GGBS on bound chloride in cement paste. In case of second group and third group (samples only with OPC), 5 faces of the samples were sealed by paraffin wax leaving one 40 mm × 40 mm face unsealed. The second group of samples were exposed in 5% Na₂SO₄ solution whereas the third group of sample were exposed in 5% MgSO₄ solution for 28, 56 and 90 days. At the end of exposure, the samples prepared for second and third groups were sliced (parallel to the exposed surface) into 10 mm thick pieces. Cement powder samples were obtained from the first group of specimens as well as from the sliced pieces obtained from the second and third group, and subsequently used for the determination of free chloride and total chloride contents, and for X-ray diffraction, Fourier transform infrared spectroscopy, and derivative thermo-gravimetric analyses. Based on the obtained results, the authors reported that the bound chlorides were released in the chloride contaminated pastes exposed to sulfate solutions. However, the release of bound chloride was more in the paste samples exposed to Na₂SO₄ solution than that exposed to MgSO₄ solution, which is partly due to the low pH in the pore solution and partly due to the blocking effect of brucite on ionic transport caused by MgSO₄. Although, fly ash and GGBS can improve the chloride binding ability, the stability of Friedel's salt is more susceptible to Na₂SO₄ attack due to the use of GGBS and especially fly ash, which is attributed to the reduction in alkalinity of the pore solution. However, the inclusion of fly ash/GGBS reduces the ingress of Na₂SO₄ thereby decreasing the attack of Na₂SO₄ on the stability of bound chlorides.

Qiao et al. [30] have investigated the effect of salt type (i.e., NaCl and MgCl₂), w/b, and supplementary cementitious materials on diffusion, wicking, and chloride binding in concrete. For this purpose, concrete mixes and cement pastes were prepared using Type I cement (ASTM C150/150M), class C fly ash, and ground blast furnace slag at different w/b such as 0.30, 0.40, 0.50, and 0.60. The fly ash and slag were used at different partial replacement levels such as 20%, 35%, and 50% by mass of total binder. The authors have carried out porosity test, and wicking test on concrete specimens of size 102 ± 2 mm in diameter and 50 ± 1 mm in thickness, whereas chloride ponding test on concrete specimens of size 102 ± 2 mm in diameter and 75 ± 1 mm in thickness. The porosity of concrete specimen was measured at the age of 91 days as per ASTM C642-13. For chloride ponding

test, all surfaces except the face of the cylindrical concrete specimens were coated with epoxy and then exposed to 5 mol/l NaCl solution for 4 months. After completion of ponding, concrete powders were obtained by grinding 2-mm layers for the first 10 mm, and 3-mm layers for depths beyond 10 mm from the exposure surface. The total chloride content of each layer was determined by the potentiometric titration. For wicking test, the circumferential surface of the cylindrical concrete specimen was coated with epoxy and the uncoated face at bottom was exposed to 5 mol/l NaCl solution or 2.5 mol/l MgCl_2 solution, and top surface was in contact with air for 5 months. Chloride binding test was carried out on the powder samples of cement paste specimens immersed in NaCl solutions (for all mixes of cement paste), and MgCl_2 solutions (for plain cement pastes) of different concentrations i.e., 0, 0.1, 0.3, 0.5, 0.7, 1.0, 1.5, 2.0, 3.0, 4.0, and 5.0 mol/l (for each solution). From the obtained results, the authors observed that the chloride binding capacity of cement paste was similar for all w/b. The replacement of cement with fly ash and slag increased the chloride binding capacity of cement paste. Further, the chloride binding was higher in the cement paste exposed to MgCl_2 solution as compared to NaCl solution. In case of concrete, the chloride penetration depth was lower in the specimens exposed to MgCl_2 solution than that exposed to NaCl solution. The authors reported that in the presence of MgCl_2 , the formation of additional reaction products in concrete may block the pores for chloride transport. The authors also reported that the wicking resulted in higher penetration depth in concrete as compared to diffusion due to the contribution of advection to the chloride transport. Further, the difference in penetration depth between diffusion and wicking was significant for concrete prepared with higher w/b.

Sharma et al. [51] have studied the influence of different cations on chloride induced rebar corrosion in mortar using electrochemical measurements. Mortar cubes of size 100 mm with a centrally embedded steel bar were prepared using Type 1 Portland cement at cement: water: sand proportion of 1: 2: 2.5. After curing for 21 days, the mortar specimens were submerged in NaCl, KCl and MgCl_2 solutions of five different concentrations i.e., 0.01 M, 0.03 M, 0.06 M, 0.1 M, and 0.15 M for 120 days. The electrochemical measurements such as open-circuit potential measurement and galvanostatic pulse technique were carried out on the steel in mortar specimens at regular intervals. Based on the obtained results, the authors reported that in mortar, the degree of corrosion of steel reinforcement was lower in case of exposure to MgCl_2 solution as compared to NaCl and KCl solutions. The lower degree of corrosion in case of exposure to MgCl_2 solution was attributed to lower amount

of free chloride ions near the rebar surface due to higher chloride binding. Further, NaCl was relatively more corrosive than KCl and MgCl_2 due to the smaller ionic radii of sodium ion with lower binding capacity of chloride that might have increased the diffusion of chloride ions.

Cheng et al. [48] have carried out an investigation to study the effect of sulfate, magnesium and composite sulfate and magnesium ion on chloride transport and chloride binding capacity in mortar made from Portland cement replaced with and without fly ash and granulated blast-furnace slag (BFS). In this study, mortar mixes were prepared using only Portland cement, cement replaced with 30% fly ash and cement replaced with 50% BFS at three w/b i.e., 0.40, 0.45, and 0.50, and constant sand to binder ratio of 3. Mortar prisms of size 40 mm $\times$ 40 mm $\times$ 160 mm were cast, and cured for 7 days. After that, four rectangular surfaces of the mortar specimens were sealed by epoxy resin, leaving two 40 mm $\times$ 40 mm faces unsealed. The specimens were exposed to different chloride and composite chloride-sulfate solutions such as NaCl, NaCl+ MgCl_2 , NaCl+ Na_2SO_4 and NaCl+ Na_2SO_4 + MgCl_2 for 60 days. At the end of exposure period, concrete powders were obtained at different depth intervals from the exposure surface by profile grinding. The obtained powder samples were used for the determination of free chloride and total chloride ion contents using potentiometric titration. The obtained chloride contents were used for the estimation of chloride binding capacity and apparent diffusion coefficient of mortar. Besides for microstructure analysis of mortar, X-Ray diffraction (XRD) analysis and thermogravimetric analysis (TGA) were carried out on mortar powder samples. The pore structure of the mortar samples was analyzed by mercury intrusion porosimetry (MIP) measurement. The obtained results showed that the presence of magnesium ions and the combined presence of magnesium and sulfate ions in the exposure solution accelerated the chloride ingress and increased the apparent chloride diffusion coefficient, while reducing the chloride binding of mortar. The sulfate ions in NaCl+ Na_2SO_4 solution decreased the diffusion of chloride ions and increased the amount of bound chloride by enhancing the formation of Friedel's salt. Further, BFS replacement significantly reduced the chloride ion diffusion coefficient and chloride binding capacity of mortar, whereas fly ash replacement had no noticeable influence on chloride ion profile and chloride binding capacity of mortar.

Yang et al. [61] have evaluated the influence of sodium sulfate and magnesium sulfate on the stability of bound chlorides in cement paste contaminated with chloride ions. In this study, cement paste specimens of size 50 mm diameter were prepared using Type II

Portland cement at w/c of 0.35. The influence of sulfate on bound chloride was investigated under three different exposure conditions. In condition I, 3% NaCl solution was added to the mixing water (deionized water) during the preparation of cement paste. The specimens were cured in saturated $\text{Ca}(\text{OH})_2$ solution for 2 months and then crushed into particles of size 0.3 ~ 3 mm. After that, the samples were dried in vacuum for 3 days and then exposed to sulfate solutions of different concentrations i.e., 1%, 5%, and 10% Na_2SO_4 solution or MgSO_4 solution for 20 weeks. In condition II, only deionized water was used in the preparation of cement paste, and then cured and crushed in the same way as condition I. The samples prepared for condition II were exposed to 3% NaCl, and combined NaCl (3%) and Na_2SO_4 (1%, 5%, and 10%) solutions or combined NaCl (3%) and MgSO_4 (1%, 5% and 10%) solutions for 20 weeks. In condition III, the specimens were prepared and cured in same manner as condition II. After that, the crushed samples were exposed to 3% NaCl solution for 8 weeks followed by 12 weeks in 1%, 5%, and 10% Na_2SO_4 solution or MgSO_4 solution. At the end of exposure, the chloride concentration of the solution was tested by ion chromatography system. Besides, the authors also performed pH measurement of host solutions, X-ray diffraction (XRD) analysis, and thermogravimetric analysis (TGA) of cement paste. Based on the results, the authors reported that the sulfate ion reduced the amount of bound chloride in cement paste and its adverse effect on chloride binding increased as the concentration of sulfate ions in the host solution increased. This is mainly caused by the decomposition of Friedel's salt in the presence of sulfate ions. For 1% sulfate concentration, the specimens exposed to Na_2SO_4 solution showed lower chloride binding than those exposed to MgSO_4 solution, whereas for 5% and 10% concentrations, MgSO_4 solution showed lower chloride binding than Na_2SO_4 solution. From the XRD and TG analyses, the authors reported that in cement paste exposed to MgSO_4 solution, at low sulfate concentration, blocking effect of brucite resulted in higher chloride binding capacity whereas at higher sulfate concentration, extensive formation of brucite and gypsum resulted in the formation of microcracks in the cement paste that increased the ingress of sulfate ions.

Chu et al. [140] have investigated the effect of cation types such as Mg^{2+} , Ca^{2+} , Na^+ , and K^+ on the stability of bound chloride ions in cement mortar exposed simultaneously under an electric field, and sulfate attack. In this study, cylindrical mortar specimens of size 100 mm in diameter and 100 mm in height with a centrally embedded steel bar (10 mm in diameter and 120 mm in length) were prepared using PII42.5 Portland cement at w/c of

0.50. After 28 days of curing, the upper and bottom surfaces of the cylindrical mortar specimens were sealed with epoxy resin. Thereafter, the mortar specimens were subjected to 24 wetting-drying cycles with one cycle consisting of 5 days of wetting in different exposure solutions followed by 2 days of drying. The exposure solutions used in this study were 5% NaCl, 5% KCl+2% Na₂SO₄, 5% NaCl+2% Na₂SO₄, 5% CaCl₂+2% Na₂SO₄ and 5% MgCl₂+2% Na₂SO₄. The authors have carried out electrochemical chloride removal (ECR) test on the mortar specimens. After the ECR test, the mortar specimens were drilled to obtain powder samples for determination of free and total chloride contents by potentiometric titration. In addition, XRD analysis and TG-DTG analysis were also carried out on the mortar samples. From the obtained results, the authors have reported that in the combined presence of electric field and sulfate attack, the bound chloride ions are unstable and prone to convert into free chloride ions. The results of XRD analysis and TG-DTG analysis indicated that the instability of bound chloride ions under an electric field was attributed to the decomposition of Friedel's salt, and desorption of physically adsorbed chloride ions in C-S-H gel. Further, the mortar specimens exposed to the solutions containing divalent cations i.e., Mg²⁺ and Ca²⁺ showed more negative effect on the stability of bound chloride ions than those exposed to the solutions containing monovalent cations i.e., Na⁺ and K⁺.

2.5 Summary of literature review

From the review of literature, it is observed that the researchers have studied the inhibition effect of different corrosion inhibitors against steel reinforcement corrosion in simulated concrete pore solution as well as in cementitious composites in the presence of aggressive ions. It is well known that chloride ions are the primary cause of steel reinforcement corrosion in concrete. Therefore, the researchers have focused on the performance of corrosion inhibitors in chloride environment.

In simulated concrete pore solution, the studies have been carried out to evaluate the inhibition effect of different corrosion inhibitors against steel reinforcement corrosion by varying the concentrations of chloride ions, and alkalinity of simulated pore solution. Further, the inhibition effect of inhibitors against corrosion of steel reinforcement in plain and blended cement extracts have also been evaluated. The inhibition efficiency of corrosion inhibitors in the studied environment were evaluated by different electrochemical tests, and microstructure analysis of steel surface. Further, various studies have been carried out by the researchers to evaluate the effectiveness of corrosion inhibitors against steel

reinforcement corrosion in cementitious composites (i.e., paste, mortar and concrete) made from different types of cement and mineral admixtures at different w/b and exposed to chloride, and combined chloride-sulfate environment. It is also observed that few studies have been conducted to evaluate the effectiveness of mixture of two inhibitors against steel reinforcement corrosion in concrete. Further, the mode of application of inhibitors i.e., as admixture and as migratory, and their effectiveness in uncracked and cracked concrete has also been studied in some of the reported research works. Besides, some studies have been carried out to evaluate the effect of corrosion inhibitors on chloride ingress, binding of chloride ions and microstructure of concrete. In addition, few studies have been carried out to compare the effectiveness of different inhibitors between simulated concrete pore solution, and cementitious composites.

From the review of literature, it is observed that a majority of earlier research work pertinent to the effectiveness of corrosion inhibitors against corrosion of steel reinforcement in concrete were carried out with the steel specimens either immersed in simulated concrete pore solutions or embedded in concrete or mortar, with sodium chloride (NaCl) as the source of chloride ions. In very few studies, calcium chloride (CaCl_2) was used as the source of chloride ions. On the other hand, it may be noted that not only NaCl but also other types of chloride salts such as KCl, CaCl_2 , and MgCl_2 are also used as deicing salts that may cause corrosion of steel reinforcement. Further, these chloride salts are also present in seawater. The cations associated with the chloride ions have different effects on the diffusion of chloride ions, chloride binding capacity, and corrosion performance of steel reinforcement in concrete.

From the review of past research studies, it is observed that the work on the effect of cation type of chloride salts on corrosion behavior of steel reinforcement in simulated concrete pore solution is limited. Further, almost no work has been reported on the effect of cation type of chloride salts on the performance of corrosion inhibitors against corrosion of steel reinforcement in concrete powder electrolyte solution, and in the concrete exposed to chloride and composite chloride-sulfate solutions. In addition, the reported research work in the literature on the effect of corrosion inhibitors on diffusion of chloride ions, chloride binding, and microstructure of cementitious composites is very little. Further, the research work on the effect of cation type of chloride salts on these properties of concrete containing corrosion inhibitors is not available in the reported literature. Besides, most of the research work focussed towards investigating the efficacy of corrosion inhibitors against steel bar

corrosion in concrete subjected to external chloride exposure conditions. However, there are very few reported research works in the literature where the efficiency of corrosion inhibitors against steel reinforcement corrosion in the presence of internal chloride has been evaluated.

The aforementioned discussion indicates that there is a need to investigate the effect of cation type of chloride salts on corrosion of steel reinforcement in concrete powder electrolyte solution in the presence of corrosion inhibitors. In addition, there is a need to study the combined effect of cation type of chloride salts and corrosion inhibitors on diffusion behavior of chloride ions, chloride binding, microstructure, and corrosion of steel reinforcement in concrete exposed to chloride and composite chloride-sulfate environment. Keeping these in view, in the present research work, an experimental study was conducted to evaluate the effect of chloride salts (associated with different cations) on corrosion behavior of steel reinforcement in both concrete powder electrolyte solution, and concrete in the presence of corrosion inhibitors. The corrosion behavior of steel reinforcement in concrete powder electrolyte solution (in the presence of chloride ions) was evaluated through potentiodynamic polarization test. Similarly, the corrosion behavior of steel reinforcement in concrete exposed to internal chloride, and external chloride and composite chloride-sulfate environment was evaluated through half-cell potential and linear polarization resistance (LPR) measurements. The compressive strength of concrete was determined to evaluate the effect of chloride ions and corrosion inhibitors on the mechanical property of concrete. Further, the effects of chloride ion concentration, and associated cation type on diffusion of chloride ions and chloride binding in concrete containing corrosion inhibitors and exposed to chloride and composite chloride-sulfate environment were also investigated. In addition, to examine the changes in microstructure of concrete in the presence of chloride ions and corrosion inhibitors, X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and Field emission scanning electron microscope (FESEM) analyses were also carried out.

2.6 Objectives

Based on the research gap in the literature, the objectives of the present research work were formulated as follows:

- To evaluate the effect of combined presence of corrosion inhibitors and chloride ions along with the associated cation type on corrosion behavior of steel reinforcement in concrete powder electrolyte solution (CPES) by carrying out potentiodynamic polarization test.
- To study the effect of cation type of admixed chloride salts on the performance of corrosion inhibitors against steel reinforcement corrosion in concrete by carrying out half-cell potential and corrosion current density measurements.
- To evaluate the effect of mix parameters (cement type and w/c), cation type of chloride salts, and sulfate ion on the effectiveness of corrosion inhibitors against steel reinforcement corrosion in concrete exposed to chloride environment vis-à-vis composite chloride-sulfate environment through corrosion parameters.
- To determine the effect of mix parameters, corrosion inhibitors, cation type of chloride salts, and sulfate ion on diffusion of chloride ions and chloride binding in concrete subjected to chloride and composite chloride-sulfate solutions.
- To analyze the microstructural changes in concrete subjected to chloride and composite chloride-sulfate environment by carrying out X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and Field emission scanning electron microscope (FESEM) analyses.

Experimental Methodology

3.1 General

In this section, details about the materials used for the preparation of concrete mixes, mix proportioning process for determination of quantities of ingredients of concrete, test specimens, and different tests performed on specimens are presented, and discussed.

3.2 Materials used

3.2.1 Cement

The cements used in the preparation of concrete specimens were ordinary Portland cement (OPC) of 43 grade complying to IS 269: 2015 [141], and ASTM C150/C150M-21 (Type I) [142]; and Portland pozzolana cement (PPC) complying to IS 1489 (Part 1): 2015 [143], and ASTM C595/C595M-21 (Type IP) [144]. The oxide composition of OPC, and PPC were determined by X-ray fluorescence (XRF) analysis, and are presented in Table 3.1. In addition, the compound composition of cements determined using Bogue's equations are also presented in Table 3.1. The physical properties of OPC, and PPC such as specific gravity (as per the guidelines of IS 4031(Part 11): 1988 [145]), and specific surface area (by nitrogen adsorption with BET method) were determined, and the obtained values are presented in Table 3.2.

Table 3.1: Chemical composition of OPC, and PPC

Oxide (weight %)	OPC	PPC
CaO	65.26	63.10
SiO ₂	21.46	23.11
Al ₂ O ₃	4.98	3.14
Fe ₂ O ₃	1.46	1.94
MgO	2.83	2.41
K ₂ O	0.41	1.12
Na ₂ O	0.83	1.16
SO ₃	2.09	2.53
Loss on ignition	2.5	1.9
Bogue composition		
Compound	OPC	PPC
Dicalcium silicate (C ₂ S)	15.83	28.75
Tricalcium silicate (C ₃ S)	61.00	50.09
Tricalcium aluminate (C ₃ A)	10.72	5.04
Tetracalcium aluminoferrite (C ₄ AF)	4.44	5.89

Table 3.2: Physical properties of OPC, and PPC

Cement	Specific surface area (m ² /kg)	Specific gravity
OPC	926	3.14
PPC	1629	2.76

3.2.2 Aggregates

Crushed aggregates of quartzite origin having two different sizes such as 20 mm MSA (maximum size of aggregate), and 10 mm MSA were used as coarse aggregates in the preparation of concrete mixes. Locally available river sand was used as fine aggregate.

3.2.2.1 Sieve analysis, and specific gravity of coarse, and fine aggregates

The sieve analysis of coarse aggregates, i.e., 20 mm MSA, and 10 mm MSA, and fine aggregate (sand) were carried out as per the guidelines stated in IS 2386 (Part-1): 1963 [146]. The particle size distribution curves of 20 mm MSA, and 10 mm MSA coarse aggregates are shown in Fig. 3.1. The particle size distribution curve of sand is shown in Fig. 3.2. From the cumulative percentage passing values obtained from sieve analysis of sand, it is observed that the sand is conforming to grading Zone-II as per IS 383: 2016 [147], and ASTM C33/C33M-18 [148]. The obtained value of fineness modulus of sand is 2.54. The specific gravity of 20 mm MSA coarse aggregate was determined using wire basket method whereas, the specific gravity of 10 mm MSA coarse aggregate, and sand were determined by pycnometer method as per the guidelines stated in IS: 2386 (Part -3): 1963 [149]. The obtained values of specific gravity for 20 mm MSA, and 10 mm MSA coarse aggregates and sand are 2.66, 2.68, and 2.65 respectively.

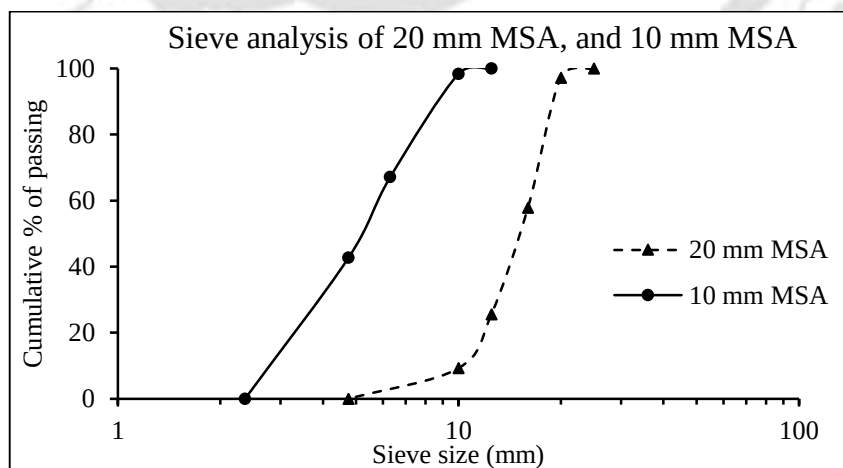


Fig. 3.1 Particle size distribution curve of 20 mm MSA, and 10 mm MSA coarse aggregates

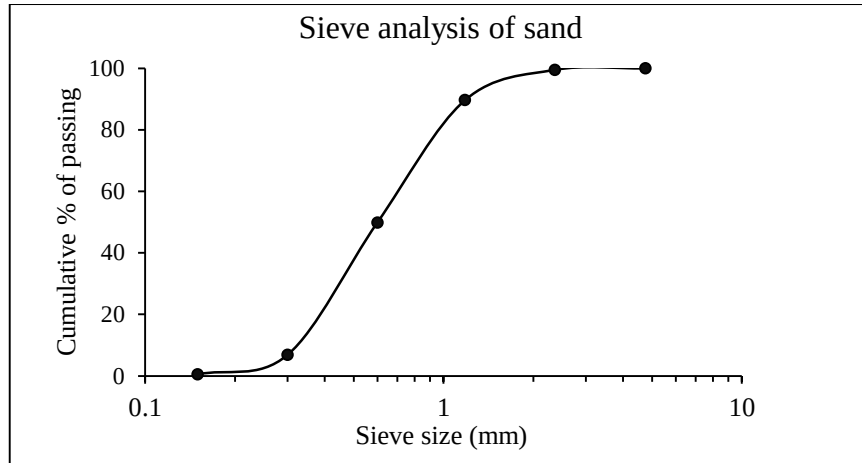


Fig. 3.2 Particle size distribution curve of fine aggregate (sand)

3.2.3 Steel

Tempcore TMT (thermomechanically treated) corrugated steel bar of diameter 12 mm was used as the steel reinforcement. The chemical composition of Tempcore TMT steel was determined by Energy-dispersive X-ray (EDX) analysis, and is shown in Table 3.3.

Table 3.3: Chemical composition of Tempcore TMT steel

Chemical element	Mn	Si	Ni	Cr	Cu	S	P	C	Fe
Weight %	1.2	0.60	0.20	0.20	0.10	0.20	0.10	<0.10	Balance

3.2.4 Chloride and sulfate salts

In the present study, three types of chloride salt such as sodium chloride (NaCl, NC), magnesium chloride (MgCl₂, MC), and calcium chloride (CaCl₂, CC) were used as the sources of chloride ions whereas magnesium sulfate (MgSO₄, MS) was used as the source of sulfate ions. In the present research work, the concentration of chloride salts admixed during the preparation of concrete mixes, and that of chloride, and sulfate salts used in the preparation of exposure solutions were selected by taking into account the concentration of these salts present in different exposure environment such as seawater, soil and groundwater as well that used in the research works reported in the literature [83, 84, 92, 109, 130, 136, 150].

3.2.5 Corrosion inhibitors

Commercially available sodium nitrite (NaNO₂, SN), and di-Sodium hydrogen phosphate (Na₂HPO₄, DHP) were used as the corrosion inhibitors in the present research work.

3.3 Mix proportioning of concrete

In the present investigation, two water-to-cement ratios (w/c) such as 0.45, and 0.55 were selected for the preparation of concrete mixes to investigate the performance of concrete against severe, and mild exposure conditions [151]. The mix quantities of different ingredients of concrete were calculated using DOE (British method) method [152] with some modification. For slump value ranging from 20 mm to 50 mm, trials concrete mixes were prepared with different water contents such as 195 kg/m³, 200 kg/m³, 205 kg/m³, and 210 kg/m³. On the basis of obtained results of slump, and 28 day compressive strength of trial mixes, a water content of 200 kg/m³ was selected in the preparation of concrete mixes. The percentage of sand (fine aggregate) was 33% by weight of total aggregate for concrete mix at w/c of 0.45, and 34% by weight of total aggregate for concrete mix at w/c of 0.55. The proportion of 10 mm MSA, and 20 mm MSA coarse aggregates was taken as 38%, and 62% respectively by weight of total coarse aggregate content for both w/c. The composition of concrete mixes at both w/c for OPC, and PPC are presented in Table 3.4.

Table 3.4: Composition of concrete mixes

Cement	Water-to-cement ratio (w/c)	Water content (kg/m ³)	Cement content (kg/m ³)	Fine aggregate content (kg/m ³)	Coarse aggregate content (kg/m ³)	
					20 mm MSA	10 mm MSA
OPC and PPC	0.45	200	444.44	574.28	723.03	443.15
	0.55	200	363.64	619.26	745.30	456.80

3.4 Experimental series

In the present research work, the experimental work was divided into three series, which are as follows:

3.4.1 Series 1

In this series, the effect of cation type of chloride salt on corrosion behaviour of steel reinforcement in concrete powder electrolyte solution (CPES) in the presence of corrosion inhibitors was evaluated. For this purpose, potentiodynamic polarization test was conducted on steel specimen (size: 12 mm diameter, and 60 mm length) in concrete powder electrolyte solution.

3.4.1.1 Preparation of concrete specimens

For this part of investigation, cube specimens of size 150 mm were prepared using OPC, and PPC concrete mixes at water-to-cement ratio (w/c) of 0.45, and admixed with chloride salts, and corrosion inhibitors. Three types of chloride salt such as sodium chloride (NaCl, NC), magnesium chloride (MgCl₂, MC), and calcium chloride (CaCl₂, CC) at the admixed concentration of 3.5% each by weight of cement were used as the sources of chloride ions. The corrosion inhibitors such as sodium nitrite (NaNO₂, SN), and di-Sodium hydrogen phosphate (Na₂HPO₄, DHP) were used at the admixed concentration of 3% each by weight of cement. The chloride salts, and corrosion inhibitors were added during the preparation of concrete mixture. The concentrations of chloride salts, and corrosion inhibitors are presented in Table 3.5. A total of 72 cube specimens were prepared from control mix, and that admixed with corrosion inhibitors, and chloride salts for determination of compressive strength, and subsequently obtaining the concrete powder samples. After 24 hours of casting, the cube specimens were demoulded, and were then placed in water curing tank for moist curing up to 28 days from the day of preparation. After completion of moist curing, compressive strength test was conducted on the cube specimens.

Table 3.5: Details of admixed chloride salts, and corrosion inhibitors in concrete mixes

Cement type	Water-to-cement ratio (w/c)	Admixed chloride salt concentration (% by weight of cement)	Admixed corrosion inhibitor concentration (% by weight of cement)
OPC, and PPC	0.45	Without any chloride salt	0% (Control)
			3% NaNO ₂
			3% DHP
		3.5% NaCl	0%
			3% NaNO ₂
			3% DHP
		3.5% MgCl ₂	0%
			3% NaNO ₂
			3% DHP
		3.5% CaCl ₂	0%
			3% NaNO ₂
			3% DHP

3.4.1.2 Preparation of steel specimens

For potentiodynamic polarization test, Tempcore TMT (thermomechanically treated) corrugated steel specimens of diameter 12 mm, and length 60 mm were used as the

reinforcing steel. The steel specimens were scrubbed using wire brush to remove any surface scale, and were then coated with epoxy, leaving an exposure length of 10 mm at both the ends. One exposed end of the specimen was immersed in the concrete powder solution during the test, whereas the opposite end was connected to the corrosion monitoring instrument. The exposed area of the steel specimen in concrete powder solution was 3.77 cm^2 . The schematic diagram, and photograph of steel specimen are illustrated in Fig. 3.3.

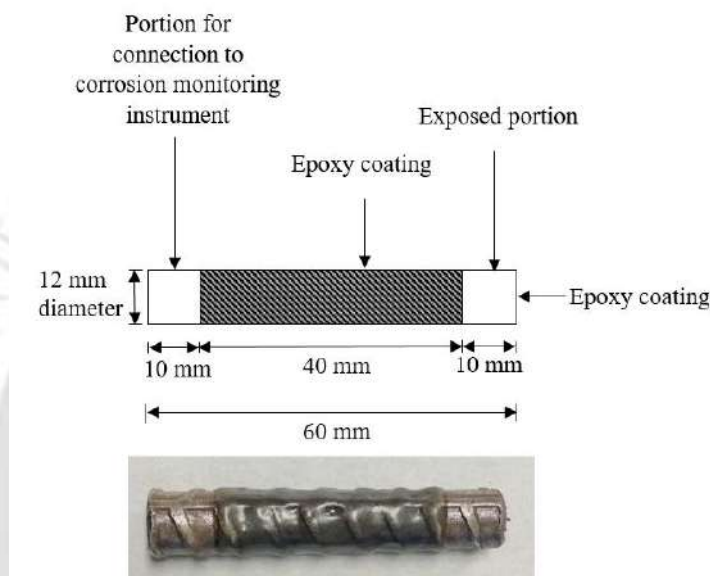


Fig. 3.3 Schematic diagram, and photograph of steel specimen

3.4.1.3 Preparation of concrete powder electrolyte solution (CPES)

To obtain the concrete powder, the crushed cube specimens, after completion of compressive strength test, were further crushed in a pulverizer. The crushed samples were then passed through a sieve having square openings of size $150 \mu\text{m}$, and the obtained powder samples were then kept in air tight containers. The concrete powder was then used for preparing the concrete powder electrolyte solution (CPES). The process of preparing the concrete powder electrolyte solution (CPES) consists of mixing the concrete powder with distilled water in the proportion of 1:1 by weight, and stirring for 25–30 min using a magnetic stirrer. Thereafter, the solution of concrete powder was simultaneously boiled, and stirred for 15–20 min using a hot plate with magnetic stirrer. The solution of concrete powder was then allowed to settle down, and cool to the room temperature. After that the solution was filtered using Whatman no.1 filter paper. This filtered solution closely represents all the species present in the concrete around the vicinity of reinforcing steel as

the solution is extracted from concrete powder, which comprises of cement hydrates, sand, coarse aggregate, and admixed concentrations of chloride salts, and corrosion inhibitors. The concrete powder electrolyte solution (CPES) was then used as the electrolyte in the potentiodynamic polarization test.

3.4.1.4 Test techniques

3.4.1.4.1 Compressive strength test

The compressive strength test was carried out at the age of 28 days from the day of casting on the cube specimens (size: 150 mm) prepared from OPC, and PPC, and admixed with or without chloride salts, and corrosion inhibitors. The obtained compressive strength values were reported as the average value of three replicate cube specimens for a given concrete mix. Along with the average value, standard deviation values of compressive strength for all the concrete mixes were also calculated.

3.4.1.4.2 Potentiodynamic polarization measurement

A corrosion monitoring instrument (make: ACM, Gill AC serial no. 1836-sequencer) was used to conduct potentiodynamic polarization test for assessing the electrochemical behaviour of steel in concrete powder electrolyte solution (CPES). The electrochemical cell with three-electrode arrangement was used for the test. The experimental setup consists of steel specimen as working electrode, an auxiliary electrode (platinum electrode), a reference electrode (saturated calomel electrode: SCE), concrete powder electrolyte solution as electrolyte, and the corrosion monitoring instrument (potentiostat). The schematic diagram, and photograph of the experimental setup are illustrated in Fig. 3.4 and Fig. 3.5 respectively. The guidelines mentioned in ASTM G5-14 [153] were followed for conducting the potentiodynamic polarization test. In this work, the potentiodynamic polarization test was performed by applying a potential scan in the range varying from 0 to 1500 mV to the steel specimen at sweep rate of 50 mV per minute, with an offset from the equilibrium potential. From the polarization test, anodic polarization curves were obtained wherein various zones of corrosion of steel reinforcement were identified.

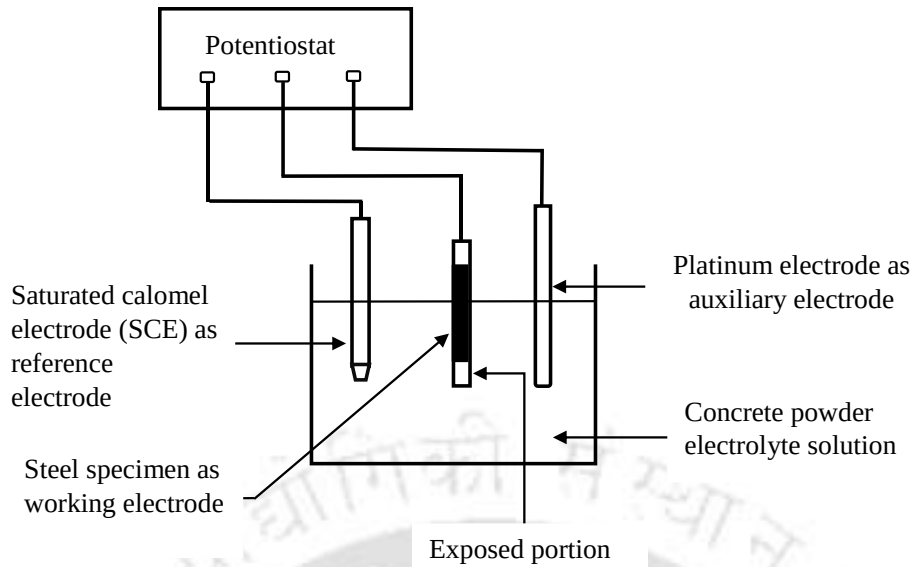


Fig. 3.4 Schematic diagram of experimental setup for potentiodynamic polarization test

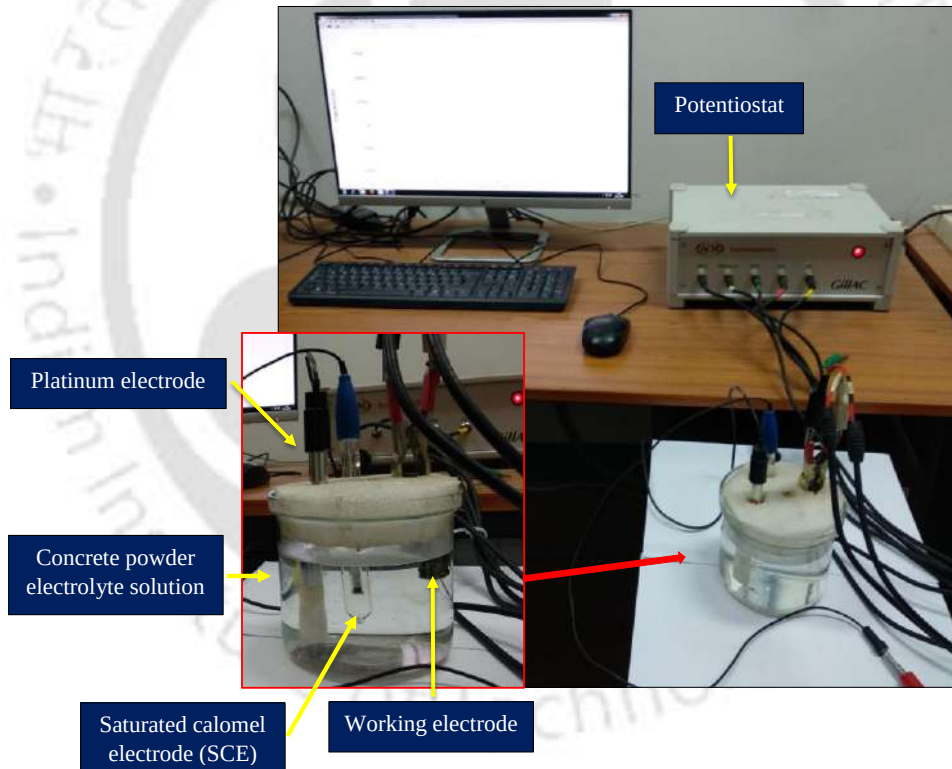


Fig. 3.5 Photograph of experimental setup for potentiodynamic polarization test

3.4.1.4.3 pH of concrete powder electrolyte solution (CPES)

The pH value of concrete powder electrolyte solution (CPES) was determined using a digital pH meter having pH range from 0 to 14. The pH meter was calibrated before measuring the pH value of concrete powder electrolyte solution.

3.4.1.4.4 Determination of chloride ion content

In this work, free chloride ion (C_F), i.e., water soluble chloride, and total chloride (C_T) ion contents of concrete powder samples obtained from OPC, and PPC concrete, and admixed with different chloride salts, and corrosion inhibitors were determined by automatic potentiometric titrator (make: Metrohm, model 848 Titrino plus). For free chloride ion content, 3 g of concrete powder, and 60 ml distilled water were taken in a 100 ml glass beaker. The mixture was then simultaneously mixed thoroughly, and gently heated on a hot plate with magnetic stirrer. Thereafter, the solution was allowed to cool to the room temperature, and free chloride ion content was then determined by titrating against 0.1 M AgNO_3 solution in the automatic titrator. To determine total chloride ion content, 3 g of concrete powder was taken in a 100 ml glass beaker, and 60 ml of 3 N nitric acid (HNO_3) was added to it. The solution was then thoroughly mixed using the magnetic stirrer, and total chloride ion content was then determined by titrating against 0.1 M AgNO_3 solution in the automatic titrator. The determined free chloride, and total chloride ion contents of concrete powder samples were expressed as percentage by weight of concrete. For each concrete mix, the bound chloride ion (C_B) content of concrete was determined by subtracting the free chloride ion content from total chloride ion content. The photograph of automatic potentiometric titrator during the test is shown in Fig. 3.6.



Fig. 3.6 Photograph of automatic potentiometric titrator during the test

3.4.1.4.5 Microstructure analysis

The concrete powder sample sieved through 75 μm sieve was used for carrying out the microstructure analysis.

3.4.1.4.5.1 X-ray diffraction (XRD) analysis

Different compounds formed in concrete mixes in the presence of chloride salts, and corrosion inhibitors were identified by X-ray diffraction (XRD) analysis. The XRD analysis was carried out in Bruker D-8 Advance X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$), and operating at 40 kV, and 40 mA. In this analysis, the concrete powder was scanned in the range varying from 5° to $55^\circ 2\theta$ at an interval of $0.05^\circ 2\theta$ per second. The obtained XRD patterns were compared with the database of standard phases to identify the presence of different compounds in concrete.

3.4.1.4.5.2 Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy was used to study the functional groups related to various compounds formed in concrete. The FTIR spectra of concrete powder samples were recorded on PerkinElmer Spectrum Two FTIR spectrometer. The concrete powder was mixed with potassium bromide (KBr) at a weight ratio of 3:250 (concrete powder to KBr), and was then compressed to obtain self-supporting pellets. Fifteen scans at a resolution of 4.0 cm^{-1} were recorded over a range of 4000 cm^{-1} to 400 cm^{-1} .

3.4.2 Series 2

This part of experimental work was designed to evaluate the effect of cation type of chloride salts on corrosion behaviour of steel reinforcement in concrete subjected to internal chloride; and external chloride, and composite chloride-sulfate exposure condition, in the presence of corrosion inhibitors. For determining corrosion parameters, half-cell potential, and linear polarization resistance (LPR) measurements were conducted on cylindrical reinforced concrete specimens (size: 72 mm diameter, and 300 mm height) with a centrally embedded steel bar.

3.4.2.1 Preparation of concrete specimens

For this part of the research work, cylindrical reinforced concrete specimens of size 72 mm diameter, and 300 mm height with a centrally embedded steel bar were prepared from different concrete mixes for half-cell potential, and linear polarization resistance (LPR) measurements. Tempcore TMT (thermomechanically treated) corrugated steel bar of

diameter 12 mm, and length 330 mm was used as the steel reinforcement. Before embedding into the cylindrical concrete specimens, the steel bars were cleaned with wire brush. After that, insulating tape was applied followed by epoxy coating over the surface of steel bar at the locations (Fig. 3.7, and Fig. 3.8), where there is a discontinuity of steel bar with surrounding concrete, to prevent crevice corrosion. The cover depth to the steel bar, and its exposed length in the cylindrical specimen were 30 mm, and 180 mm respectively as shown in Fig. 3.8. All the cylindrical specimens were admixed with corrosion inhibitors, i.e., sodium nitrite, and di-Sodium hydrogen phosphate at the given concentration (discussed afterward) during the time of preparation. The cylindrical concrete specimens were demoulded after 24 hours of casting, and were then cured in water till the age of 28 days.

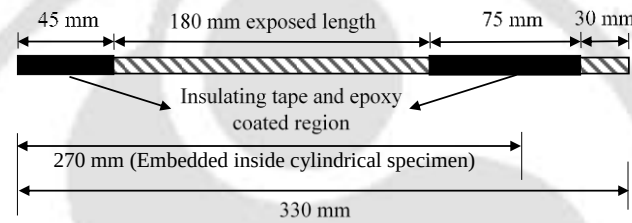


Fig. 3.7 Schematic diagram of steel bar of diameter 12 mm

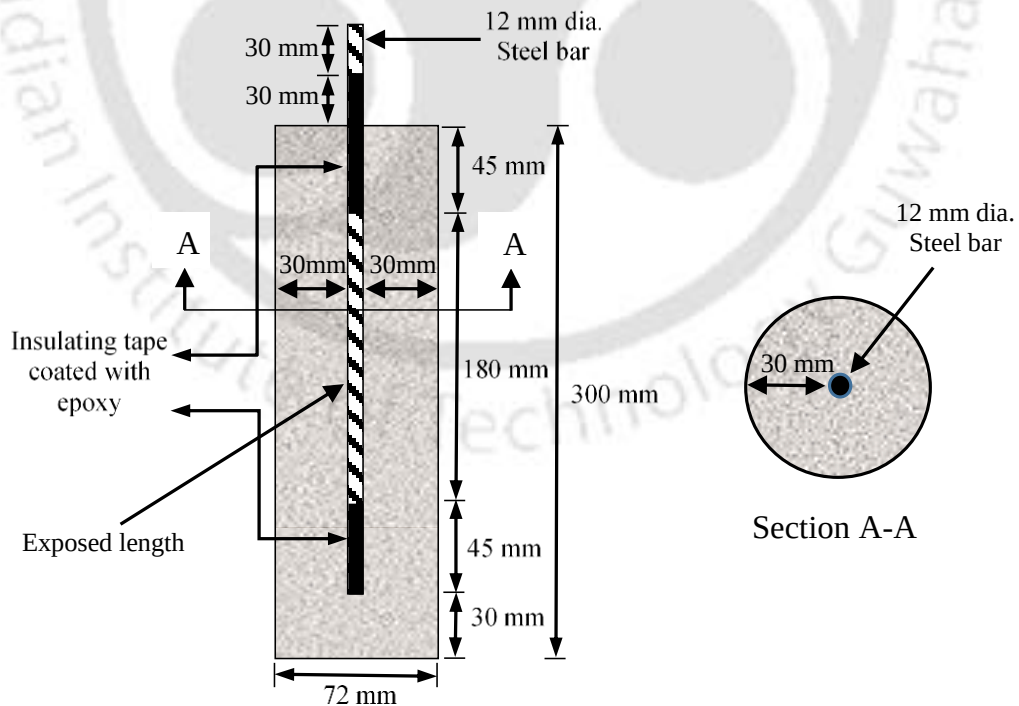


Fig. 3.8 Schematic diagram of cylindrical reinforced concrete specimen of diameter 72 mm and height 300 mm

3.4.2.2 Exposure conditions

3.4.2.2.1 Internal exposure

For internal exposure condition, three types of chloride salt such as sodium chloride (NaCl), magnesium chloride (MgCl_2), and calcium chloride (CaCl_2) were added in the mixing water at the concentration of 3.5% each by weight of cement during the preparation of concrete mixes. Further, corrosion inhibitors, i.e., sodium nitrite, and di-Sodium hydrogen phosphate were also added in the mixing water at the concentration of 3% each by weight of cement. By taking into account the cement type, w/c, and admixed concentrations of chloride salts, and corrosion inhibitors, a total of 18 concrete mixes were prepared for internal chloride exposure. With three replicate cylindrical specimens from each mix, a total of 54 specimens were prepared from all the concrete mixes for internal chloride exposure. The details of concrete mixes prepared for internal chloride exposure are presented in Table 3.6. After completion of water curing, the cylindrical reinforced concrete specimens admixed with chloride salts, and corrosion inhibitors were kept in ambient laboratory condition for a period of 826 days.

Table 3.6: Details of concrete mixes prepared for internal chloride exposure condition

Cement type	Water-to-cement ratio (w/c)	Admixed chloride salt concentration (% by weight of cement)	Admixed corrosion inhibitor concentration (% by weight of cement)
OPC, and PPC	0.45	3.5% NaCl	0%
			3% NaNO_2
			3% DHP
		3.5% MgCl_2	0%
			3% NaNO_2
			3% DHP
		3.5% CaCl_2	0%
			3% NaNO_2
			3% DHP

3.4.2.2.2 External exposure

The cylindrical reinforced concrete specimens prepared separately for external exposure condition, i.e., prepared with corrosion inhibitors, and without chloride salts, were kept in ambient laboratory condition for 7 days, after completion of water curing. After that, the cylindrical specimens were subjected to external chloride, and composite chloride-sulfate solutions with alternating wetting-drying cycles. The chloride exposure solutions were

prepared using chloride salts such as sodium chloride of concentrations 1.5%, 3.5%, and 5.5%, magnesium chloride of concentration 3.5%, and calcium chloride of concentration 3.5%. The combined chloride-sulfate exposure solutions were prepared using combinations of chloride salt (NaCl or MgCl₂ or CaCl₂) of concentration 3.5%, and magnesium sulfate (MgSO₄) of concentration 3.5%. Thus, 8 types of solution were used for external exposure condition. By taking into account the cement type, w/c, and admixed concentrations of corrosion inhibitors, a total of 20 concrete mixes were prepared for external exposure. With three replicate cylindrical specimens from each mix, a total of 354 specimens were prepared from all the concrete mixes for external exposure condition. From 354 cylindrical reinforced concrete specimens, 300 specimens were used for chloride exposure, and 54 specimens were used for composite chloride-sulfate exposure. The details of concrete mixes prepared for external exposure, and the exposure solutions are shown in Table 3.7. The photograph of the cylindrical reinforced concrete specimens subjected to exposure solutions is shown in Fig. 3.9. In the present study, one wetting-drying cycle consists of 7 days of wetting followed by 14 days of laboratory drying. During the wetting period, the cylindrical reinforced concrete specimens were partially immersed in different exposure solutions in plastic containers up to a height of 260 mm from bottom. The exposure of the specimens to the solutions was continued for 39 wetting-drying cycles (i.e., 819 days).

Table 3.7: Details of concrete mixes prepared for external exposure, and the exposure solutions

Cement type	Water-to-cement ratio (w/c)	Admixed corrosion inhibitor concentration (% by weight of cement)	Exposure solutions
OPC, and PPC	0.45, and 0.55	0%; and 1% and 3% each for NaNO ₂ and DHP	1.5% NaCl
			3.5% NaCl
			5.5% NaCl
			3.5% MgCl ₂
			3.5% CaCl ₂
	0.45	0%; and 3% each for NaNO ₂ and DHP	3.5% NaCl+3.5% MgSO ₄
			3.5% MgCl ₂ +3.5% MgSO ₄
			3.5% CaCl ₂ +3.5% MgSO ₄



Fig. 3.9 Photograph of cylindrical reinforced concrete specimens subjected to exposure solutions

3.4.2.3 Test techniques

3.4.2.3.1 Corrosion measurements

Half-cell potential (HCP), and linear polarization resistance (LPR) measurements were carried out on the cylindrical reinforced concrete specimens subjected to internal, and external exposure conditions using the corrosion monitoring instrument (make: ACM, Gill AC serial no. 1836-sequencer). For external exposure condition, the corrosion measurements were carried out first at the end of 3rd wetting-drying cycle, i.e., at the age of 98 days from the day of casting. Thereafter, the corrosion measurements were carried out at regular intervals of 6 wetting-drying cycles, i.e., at the end of every 126 days interval up to 476 days from the day of casting. After 476 days, the corrosion measurements were carried out at regular intervals of 3 wetting-drying cycles, i.e., at the end of every 63 days interval till 854 days from the day of casting (i.e., till 819 days from start of exposure). Out of three replicate cylindrical reinforced concrete specimens of a given concrete mix, the exposure to the solutions was discontinued for two replicate specimens when the half-cell potential value continued more negative than -270 mV (SCE) at the end of very next wetting-drying cycle after it became more negative than -270 mV (SCE) at a given testing cycle. Subsequently, these two replicate specimens from each concrete mix were drilled to collect the concrete powder samples from near the rebar level (i.e., from depth interval of 25-30 mm from the exposure surface), which were further used for determining the free chloride ion (C_F) content, total chloride ion (C_T) content, and for performing the microstructures analysis. The exposure to the solutions, and corrosion tests on the remaining replicate cylindrical reinforced concrete specimen were continued till 819 days from the start of exposure. For internal exposure condition, the corrosion tests were

performed first at the age of 98 days from the day of casting, and thereafter, at the end of every 126 days interval up to 854 days on all the three replicate cylindrical reinforced concrete specimens of a given concrete mix. The schematic diagram, and photograph of experimental setup for measurement of corrosion parameters, i.e., half-cell potential, and corrosion current density (by LPR measurement) of steel reinforcement are shown in Fig. 3.10, and Fig. 3.11 respectively. The experimental setup consists of a plastic container filled with the test solution, embedded steel bar in the cylindrical specimen as working electrode, a pair of stainless steel plates as auxiliary electrode, saturated calomel electrode (SCE) as reference electrode, and potentiostat (corrosion monitoring instrument). During testing of specimens exposed to external solutions, the test solution in the plastic container was same as the exposure solution i.e., chloride solution or composite chloride-sulfate solution. During testing of specimens exposed to internal chloride, the test solution in the plastic container was water. During testing, the cylindrical specimen was partially immersed in the test solution up to a height of 260 mm from bottom in the container (Fig. 3.10). The half-cell potential of steel reinforcement was measured with reference to saturated calomel electrode (SCE). During linear polarization resistance (LPR) measurement, the reinforcing steel bar was polarized to ± 20 mV from corrosion potential at a scan rate of 6 mV/min. The polarization resistance (R_p) of steel reinforcement was determined, and it was used for determining the corrosion current density (I_{corr}) of steel reinforcement using the Stern–Geary equation [1]: The corrosion current density (I_{corr}) of steel reinforcement was determined using the Stern–Geary equation [1]:

$$I_{corr} = \frac{B}{R_p} \quad 3.1$$

Where, B is the Stern-Geary constant, and R_p is the polarization resistance of steel reinforcement. The Stern-Geary constant is calculated from the following expression [17]:

$$B = \frac{(\beta_a \times \beta_c)}{2.30(\beta_a + \beta_c)} \quad 3.2$$

Where, β_a , and β_c are anodic, and cathodic Tafel constants respectively. The value of B is generally taken as 26 mV, and 52 mV for steel reinforcement in active state, and passive state respectively [1]. In this study, the value of B was taken as 26 mV considering the steel reinforcement in active condition.

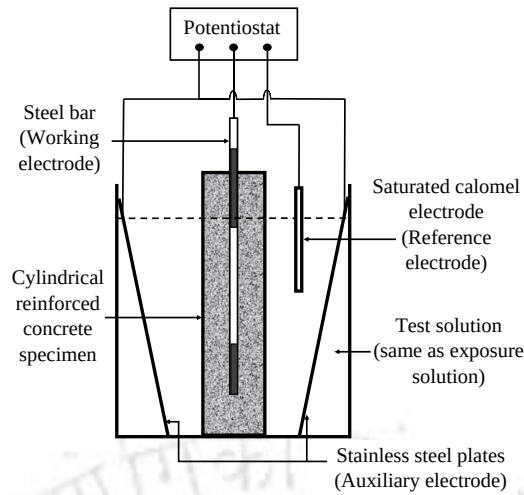


Fig. 3.10 Schematic diagram of test setup for half-cell potential, and corrosion current density measurements

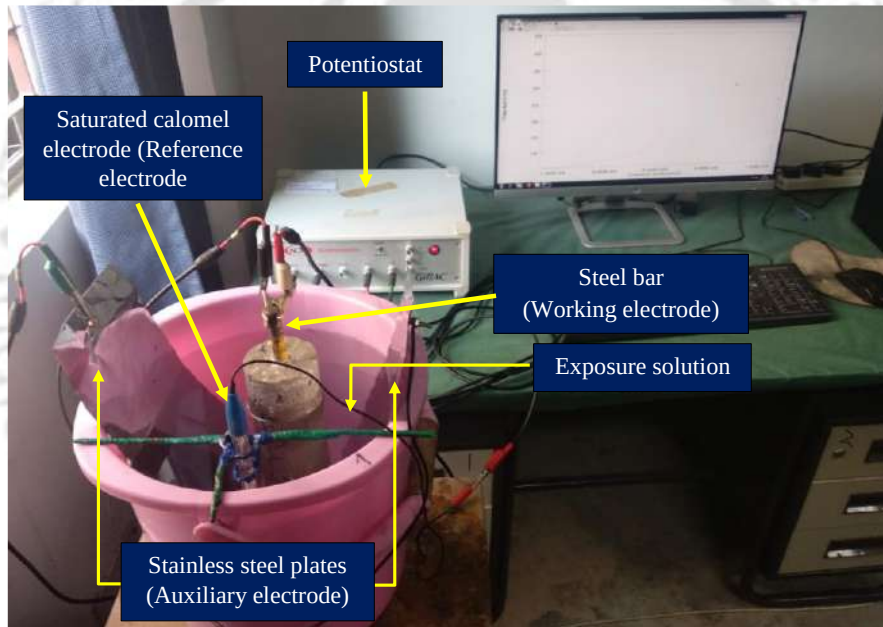


Fig. 3.11 Photograph of test setup for half-cell potential, and corrosion current density measurements

3.4.2.3.2 Collection of concrete powder

After completion of half-cell potential (HCP), and linear polarization resistance (LPR) measurements, concrete powder samples were collected from the cylindrical reinforced concrete specimens exposed to internal, and external exposure conditions by drilling process. The concrete powder samples were collected from near the rebar level i.e., from depth interval of 25-30 mm from the exposure surface of cylindrical specimen by drilling in radial direction on four longitudinal faces of the specimen. Subsequently, the drilled

concrete powder samples collected from four sides of the cylindrical specimen were mixed to obtain the concrete powder sample at depth interval of 25-30 mm from the exposure surface, which represents the concrete powder sample near rebar level. It may be noted that the concrete cover to the rebar in the cylindrical specimen was 30 mm. The collected concrete powder samples were stored in air tight containers, and were subsequently used to determine the free chloride ion content, total chloride ion content, and for carrying out the microstructure analysis of concrete. The photographs of drilled cylindrical reinforced concrete specimens, and the collected concrete powder samples are shown in Fig. 3.12, and Fig. 3.13 respectively.



Fig. 3.12 Photograph of the drilled cylindrical reinforced concrete specimens



Fig. 3.13 Photograph of concrete powder samples obtained from the rebar level (25-30 mm) of cylindrical reinforced concrete specimen

3.4.2.3.3 Chloride content

The chloride content, i.e., free chloride ion (C_F) content, and total chloride ion (C_T) content of concrete powder samples obtained from near the rebar level (i.e., from depth interval of 25-30 mm from the exposure surface) of cylindrical specimens were determined by potentiometric titration using an automatic titrator (make: Metrohm, model 848 Titrino plus). The procedure used for determining the free chloride ion content, and total chloride ion content of concrete is already described in section 3.4.1.4.4. The chloride contents of concrete powder samples were determined as percentage by weight of concrete. For each concrete mix, the bound chloride ion (C_B) content was determined as the difference of total chloride ion content, and free chloride ion content.

3.4.2.3.4 Microstructure analysis

The concrete powder samples obtained from near the rebar level of cylindrical specimens were sieved through 75 μm sieve, and were subsequently used for carrying out the microstructure analysis.

3.4.2.3.4.1 X-ray diffraction (XRD) analysis

The XRD analysis of concrete powder sample was conducted using Rigaku SmartLab 9KW X-ray diffractometer. The XRD patterns were recorded between 5° to 55° 2θ at step length of 0.03° 2θ . The obtained XRD patterns of concrete powder samples were compared with standard database to identify the phase composition of concrete. From the obtained XRD patterns, the weight (%) of compounds namely ettringite (E), calcium chloroaluminate (CCA), portlandite (CH), calcium carbonate (CCB), and quartz (Q) were estimated from semi-quantification analysis using reference intensity ratio (RIR) matrix-flushing method [154, 155]. The weight (%) of the compounds present in concrete mixes were estimated using the following equation [47, 133]:

$$W_i = \frac{\frac{I_i}{RIR_i}}{\sum_{i=1}^N \left(\frac{I_i}{RIR_i} \right)} \quad 3.3$$

$$W_1 + W_2 + \dots + W_N = 1 \quad 3.4$$

Where W_i = relative mass of compound i ,

I_i = integral intensity of the highest peak of compound i (determined using PANalytical X'PertHighScore Plus software), RIR_i = reference intensity ratio of compound i (mentioned

in PDF reference library of International Centre for Diffraction Data (ICDD)), N = number of compounds considered in the sample.

For consistent use of RIR concentrations among the samples, the reference phase corresponding to a given compound was kept same for all the samples. The details about the compounds used in the semi-quantification analysis are obtained from the International Centre for Diffraction Data (ICDD) reference library, and are shown in Table 3.8.

Table 3.8: Details of compounds obtained from PDF card of International Centre for Diffraction Data (ICDD)

Phase name	Abbreviation	PDF card number	RIR
Ettringite	E	01-072-0646	1.61
Calcium chloroaluminate	CCA	01-078-1219	1.36
Portlandite	CH	00-004-0733	1.40
Calcite	CCB	00-005-0586	2.00
Quartz	Q	00-046-1045	3.41

3.4.2.3.4.2 Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy was carried out on the concrete powder samples collected from cylindrical specimens in PerkinElmer Spectrum Two FTIR spectrometer, and the procedure is already described in section 3.4.1.4.5.2.

3.4.2.3.4.3 Field emission scanning electron microscope (FESEM) analysis

To study the surface morphology of concrete, FESEM analysis was performed on concrete powder samples collected from cylindrical specimens, using Zeiss Sigma 300 field emission scanning electron microscope. The concrete powder sample was mounted on an aluminum stub using carbon tape, and the sample was then coated with a thin layer of gold by sputtering method. The FESEM images were obtained using in-lens mode.

3.4.3 Series 3

This part of experimental work was designed to investigate the effect of cation type of chloride salt, and corrosion inhibitor on free chloride ion content, chloride diffusion coefficient, and chloride binding capacity of concrete exposed to chloride, and composite chloride-sulfate solutions.

3.4.3.1 Preparation of concrete cubes

For this part of experimental study, replicate cube specimens of size 150 mm were prepared from OPC, and PPC concrete mixes at w/c of 0.45, and 0.55. Corrosion inhibitors, i.e., sodium nitrite (NaNO_2), and di-Sodium hydrogen phosphate (DHP) were added in the mixing water at the concentration of 3% each by weight of cement during the time of preparation of concrete mixes. By taking into account the cement type, w/c, and admixed concentrations of corrosion inhibitors, a total of 12 concrete mixes were prepared for external exposure. Fifteen replicate cube specimens (3 replicate cubes for 28 days compressive strength test, and 12 replicate cubes for external exposure) were cast from each concrete mix. The cube specimens were demoulded after 24 hours of preparation, and were then cured in water till 28 days.

3.4.3.2 Exposure condition

After completion of moist curing, three replicate cube specimens from each mix were tested for determining the 28 days compressive strength of concrete, and the remaining replicate cube specimens were kept in laboratory dry condition for 7 days. Toward the end of drying period, the surfaces of the concrete cubes were cleaned using wire brush to remove any dust present on the surface. After that, four vertical faces of each cube were applied with epoxy coating, leaving two opposite faces exposed. A plastic reservoir of size 100 mm $\times$ 100 mm $\times$ 50 mm was attached on one of the uncoated faces (considered as top face) of the concrete cube by epoxy coating for ponding with different exposure solutions. The region outside the reservoir on top face of the cube specimen was also applied with epoxy coating. The schematic diagram, and photograph of the concrete cube specimen with the plastic reservoir is shown in Fig. 3.14. After completion of initial drying period of 7 days, the cube specimens were subjected to chloride, and composite chloride-sulfate solutions with alternating wetting-drying cycles with one cycle consisting of 7 days of wetting followed by 14 days of drying. During wetting period, the plastic reservoirs were filled with chloride, and composite chloride-sulfate solutions up to a height of 40 mm. Chloride solutions containing 1.5%, 3.5%, and 5.5% each of NaCl , MgCl_2 , and CaCl_2 , and composite chloride-sulfate solutions containing 3.5% NaCl +3.5% MgSO_4 , 3.5% MgCl_2 +3.5% MgSO_4 , and 3.5% CaCl_2 +3.5% MgSO_4 were used as the exposure solutions. The details of exposure solutions are presented in Table 3.9. The reservoirs were covered with plastic sheets to avoid evaporation of the solution during wetting period. During drying period, the solutions were taken out from the reservoir, and the cube specimens were kept under ambient

laboratory dry condition. The cube specimens of different concrete mixes were exposed to chloride, and composite chloride-sulfate solutions for a period of 756 days (36 cycles), and the exposure solutions were replenished with fresh solutions at the start of every wetting-drying cycle. The photograph of cube specimens subjected to exposure solutions is shown in Fig. 3.15.

Table 3.9: Details of exposure solutions

Cement type	Water-to-cement ratio (w/c)	Admixed corrosion inhibitor concentration (% by weight of cement)	Exposure solution
OPC, and PPC	0.45, and 0.55	0%; and 3% each for NaNO_2 and DHP	1.5%, 3.5%, and 5.5% NaCl
			1.5%, 3.5%, and 5.5% MgCl_2
			1.5%, 3.5%, and 5.5% CaCl_2
			3.5% NaCl+3.5% MgSO_4
			3.5% CaCl_2 +3.5% MgSO_4
			3.5% MgCl_2 +3.5% MgSO_4

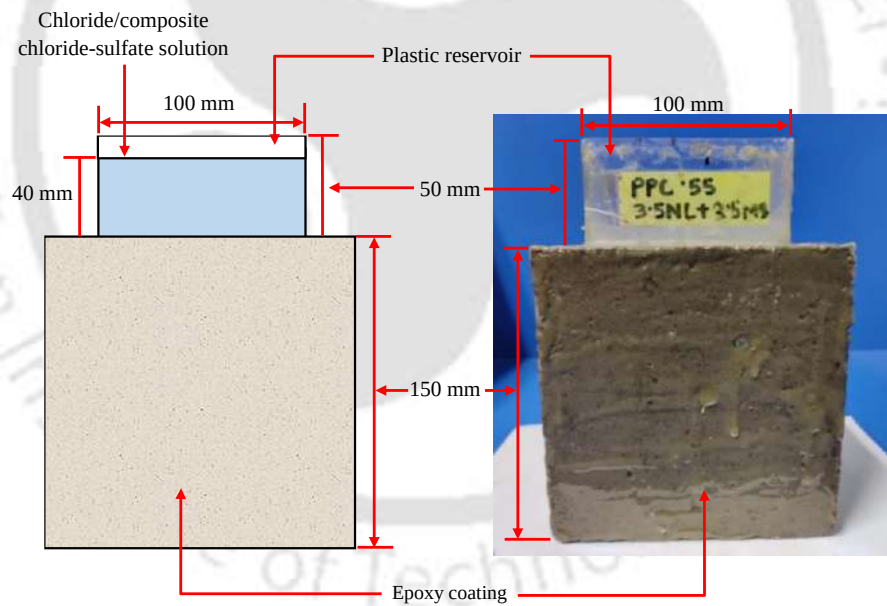


Fig. 3.14 Schematic diagram, and photograph of the cube specimen exposed to chloride, and composite chloride-sulfate solution



Fig. 3.15. Photograph of cube specimens subjected to alternating wetting-drying cycles

3.4.3.3 Test Techniques

3.4.3.3.1 Compressive strength test

The compressive strength of cubes made from OPC, and PPC control mixes (without corrosion inhibitors), and those admixed with corrosion inhibitors at w/c of 0.45, and 0.55 were determined at the age of 28 days from the day of casting.

3.4.3.3.2 Concrete powder sample collection, and determination of chloride content

Concrete powder samples were collected from the cubes at the end of exposure, i.e., after 756 days of exposure, using a drilling machine. The top surface of cube specimen, which was exposed to the chloride solution or composite chloride-sulfate solution was cleaned to remove any salt deposits, and subsequently drilled at 10 depth intervals each of 5 mm from the top surface, i.e., up to a depth of 50 mm to collect the concrete powder samples. The collected concrete powder samples were used for the determination of free chloride ion (C_F), and total chloride ion (C_T) contents. Potentiometric titration (already described in Section 3.4.1.4.4) was used for determining C_F , and C_T contents of concrete powder samples obtained from various depth intervals of concrete cubes prepared from OPC, and PPC containing different corrosion inhibitors, and exposed to chloride, and composite chloride-sulfate solutions. The measured chloride contents, i.e., C_F , and C_T of concrete powder samples were represented as percentage by weight of concrete. The measured chloride content of a given depth interval of cube specimen is considered as the average value corresponding to the concrete powder sample obtained from that depth interval. In the free chloride profile, the obtained free chloride ion contents for different depth intervals

are represented at their respective mid depths e.g., at 2.5 mm for depth interval of 0–5 mm. The photographs of drilled concrete cube specimens, and collected concrete powder samples are shown in Fig. 3.16, and Fig. 3.17 respectively.



Fig. 3.16 Photograph of drilled concrete specimens



Fig. 3.17 Photograph of concrete powder samples obtained from different depth intervals

3.4.3.3.3 Determination of apparent chloride diffusion coefficient of concrete

Chloride diffusion coefficient indicates the rate of ingress of chloride ions through the concrete. Diffusion of chloride ions in concrete is commonly described by Fick's second law of diffusion, and the apparent diffusion coefficient (D_{app}) was calculated using Eq. 3.5 as per ASTM C1556-11a [156].

$$C_{(x,t)} = C_s \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{D_{app}t}} \right) \right] \quad 3.5$$

Where, $C = C_{(x,t)}$ denotes the chloride ion content (%) as a function of x (depth from exposure surface), and t (exposure period), C_s represents the apparent surface chloride ion content (%), and erf is the Gauss error function.

In case of concrete undergoing alternating wetting-drying cycles, the transport of chloride ions in the surface layer of concrete cover is influenced by both diffusion, and convection, often known as convection zone [157-159]. Generally, the extent of convection zone is considered from the exposure surface to the location where the concentration of chloride ions is maximum [157]. In this region, the convection process plays a dominant role in chloride transport over the diffusion process whereas, beyond the convection zone, i.e., in the inner part of concrete, diffusion plays a dominant role in the process of chloride transport [158, 159]. The Eq. 3.5 is applicable where the chloride transport is governed by diffusion only [157]. However, in the present study, existence of convection zone was observed in some of the concrete specimens subjected to alternating wetting-drying cycles. Therefore, in case of presence of convection zone, the chloride content in the convection zone needs to be excluded while applying the Fick's second law of diffusion. By taking into account the depth of the convection zone (x_c), the chloride content profile of concrete beyond convection zone (i.e., in diffusion zone) can be expressed as follows [157, 159, 160]:

$$C_{(x,t)} = C_{smax} \left[1 - \operatorname{erf} \left(\frac{x-x_c}{2\sqrt{D_{app}t}} \right) \right] \quad 3.6$$

Where, C_{smax} represents the peak chloride content in the chloride profile (i.e., at the interface of convection zone, and diffusion zone).

To obtain the apparent surface chloride ion content (C_s), and apparent chloride diffusion coefficient (D_{app}) of concrete, the generalized reduced gradient (GRG) nonlinear solving method was used to solve the above equations using SOLVER function of Microsoft Excel spreadsheet [161].

3.4.3.3.4 Determination of chloride binding capacity of concrete

Chloride binding capacity of concrete is considered as one of the major factors in mitigating the ingress of chloride ions into concrete structures subjected to exposure environment [43]. When chloride ions from the exposure environment enter into the concrete, a portion of them are captured by the cement hydration products, which is called as chloride binding [44]. Chloride binding capacity can be defined as shown in Eq. 3.7 [50].

$$R = \frac{\partial C_B}{\partial C_F} \quad 3.7$$

Where R = chloride binding capacity, C_F = free chloride ion content, C_B = bound chloride ion content. By fitting the experimentally obtained free chloride ion (C_F) content, and total chloride ion (C_T) content, it is observed that there exists a linear relation between C_F , and C_T contents. The linear relationship between C_F , and C_T contents is given by [50]:

$$C_T = \alpha C_F + \beta \quad 3.8$$

Where, α , and β are binding constants.

The chloride binding capacity (R) is calculated as follows [50, 162]:

$$R = \alpha - 1 \quad 3.9$$

Further, modified Langmuir, and Freundlich isotherms were applied to the obtained free chloride (% by weight of concrete), and bound chloride (% by weight of concrete). The bound chloride (% by weight of concrete) was calculated as the difference of total chloride ion content, and free chloride ion content. It may be noted that while applying modified Langmuir, and Freundlich binding isotherms in the present study, the free chloride was not expressed in mole/l of pore solution as the same was not determined through pore solution expression method, or equilibrium method.

The modified binding isotherms are as follows [27]:

Langmuir binding isotherm:

$$C_B = \frac{\alpha C_F}{(1 + \beta C_F)} \quad 3.10$$

Where C_F = free chloride ion content, C_B = bound chloride ion content, and α , and β are binding constants.

Freundlich binding isotherm:

$$C_B = \alpha C_F^\beta \quad 3.11$$

Where C_F = free chloride ion content, C_B = bound chloride ion content, and α , and β are binding constants.

3.4.3.3.5 Microstructure analysis of concrete powder

The microstructure study was carried out on the concrete powder samples collected from OPC, and PPC control concrete cubes, and those admixed with corrosion inhibitors, and exposed to chloride, and composite chloride-sulfate solutions by X-ray diffraction (XRD) analysis, Fourier transform infrared (FTIR) spectroscopy, and Field emission scanning

electron microscope (FESEM) analysis. For microstructure analysis, the concrete powder samples collected from different depth intervals of cube specimens were sieved through 75 μm sieve, and stored in air tight containers. The procedures described in section 3.4.2.3.4 were used for performing XRD, FTIR, and FESEM analyses on the concrete powder samples.

3.5 Summary

In the present study, concrete mixes were prepared using OPC, and PPC at w/c of 0.45, and 0.55. Corrosion inhibitors such as sodium nitrite (NaNO_2), and di-Sodium hydrogen phosphate were admixed at two concentrations, i.e., 1%, and 3% by weight of cement during the preparation of concrete mixes. Three types of chloride salt such as sodium chloride (NaCl), magnesium chloride (MgCl_2), and calcium chloride (CaCl_2) were used as the sources of chloride ions, and magnesium sulfate (MgSO_4) was used as the source of sulfate ions. Concrete cubes (size: 150 mm), and cylindrical reinforced concrete specimens (size: 72 mm diameter, and 300 mm height) with a centrally embedded steel bar of 12 mm diameter were prepared from different concrete mixes, and were subjected to internal chloride exposure, and external chloride, and composite chloride-sulfate exposure conditions. The corrosion behavior of steel reinforcement was evaluated through potentiodynamic polarization, half-cell potential, and linear polarization resistance measurements. At the end of exposure period, free chloride ion, and total chloride ion contents of concrete mixes admixed with, and without corrosion inhibitors, and exposed to internal chloride, and external chloride, and composite chloride-sulfate solutions were determined. From the obtained free chloride content profile, the apparent chloride diffusion coefficient of concrete was determined in case of exposure to external chloride, and composite chloride-sulfate solutions. In addition, the chloride binding capacity of concrete exposed to chloride, and composite chloride-sulfate exposure solutions was also determined. Further, microstructure analysis such as XRD analysis, FTIR analysis, and FESEM analysis were carried out on the concrete powder samples collected from cube, and cylindrical reinforced concrete specimens.

Effect of Cation Type of Chloride Salts on Corrosion Behaviour of Steel Reinforcement in Concrete Powder Electrolyte Solution in the Presence of Corrosion Inhibitors

4.1 General

In this chapter, the results obtained from the potentiodynamic polarization test on steel reinforcement in concrete powder electrolyte solution (CPES) containing chloride salts (sodium chloride, magnesium chloride, and calcium chloride) and corrosion inhibitors (sodium nitrite and di-Sodium hydrogen phosphate) are presented, and discussed. The compressive strength of concrete was determined to evaluate the effect of chloride ions, and corrosion inhibitors on the mechanical property of concrete. Further, the effect of cation type of chloride salts on free chloride ion content and chloride binding in concrete were investigated. In addition, to examine the phase composition changes of hardened concrete in the presence of chloride ions, and corrosion inhibitors, X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy analyses were also carried out, and the obtained results are presented and described in this chapter.

4.2 Compressive strength of concrete

The 28 days compressive strength values of concrete cube specimens made from OPC and PPC at w/c of 0.45, and admixed with and without chloride salts, and corrosion inhibitors are presented in Table 4.1. The values presented in Table 4.1 are the average compressive strength of three replicate cube specimens from a given concrete mix. Along with the average value, standard deviation values of compressive strength for all the concrete mixes were also calculated, and are shown in Table 4.1. The obtained pH values of concrete mixes are also presented in Table 4.1. From the average compressive strength, and standard deviation values, it is observed that the OPC concrete showed higher compressive strength than PPC concrete in both control specimens as well as in the specimens admixed with corrosion inhibitors, chloride salts, and chloride salts plus corrosion inhibitors, as evident from Table 4.1. The higher compressive strength of OPC concrete may be attributed to the significant effect of hydration reaction than that of pozzolanic reaction in PPC concrete in enhancing the compressive strength till the age of 28 days [163, 164].

Table 4.1 Compressive strength, and pH of concrete made with w/c of 0.45

Cement type	Admixed chloride salt concentration	Admixed corrosion inhibitor concentration	Compressive strength (N/mm ²)	Standard deviation (N/mm ²)	pH
OPC	0%	0% (Control)	42.81	0.55	13.26
		3% NaNO ₂	36.60	0.91	13.64
		3% DHP	28.30	1.50	13.78
	3.5% NaCl	0%	43.10	0.55	12.84
		3% NaNO ₂	41.19	0.76	12.98
		3% DHP	26.67	1.81	13.08
	3.5% MgCl ₂	0%	50.81	0.55	12.50
		3% NaNO ₂	42.37	0.91	12.59
		3% DHP	34.67	0.96	12.73
	3.5% CaCl ₂	0%	56.30	1.04	12.66
		3% NaNO ₂	52.00	0.96	12.70
		3% DHP	39.85	0.76	12.80
PPC	0%	0% (Control)	37.04	0.55	12.91
		3% NaNO ₂	36.44	1.30	13.08
		3% DHP	24.00	0.36	13.26
	3.5% NaCl	0%	41.63	0.42	12.60
		3% NaNO ₂	40.30	1.37	12.73
		3% DHP	25.04	1.16	12.89
	3.5% MgCl ₂	0%	42.37	1.99	12.40
		3% NaNO ₂	40.44	1.66	12.46
		3% DHP	30.07	1.16	12.61
	3.5% CaCl ₂	0%	52.30	0.91	12.53
		3% NaNO ₂	50.96	1.51	12.69
		3% DHP	38.37	0.55	12.78

4.2.1 Influence of cation type of chloride salts on compressive strength of concrete

From the average compressive strength, and standard deviation values, it is inferred that the chloride admixed concrete mixes showed higher compressive strength than control mix irrespective of cement type, and cation type of chloride salts, as evident from Table 4.1. This shows that the presence of chloride salts accelerated the cement hydration reaction thereby resulting in higher compressive strength of concrete [165-167]. While comparing the effect of cation type of chloride salts on compressive strength, it is observed that the concrete mixes admixed with CaCl₂ exhibited higher compressive strength followed by

MgCl₂, and NaCl irrespective of cement type. This indicates that CaCl₂ accelerated the strength development process of concrete to a greater extent than MgCl₂, and NaCl. In addition, the higher compressive strength of concrete mix admixed with CaCl₂ may also be attributed to the filling of pores with calcium chloroaluminate (CCA: the product of reaction between chloride ions, and C₃A) to a greater extent than that in case of concrete mixes admixed with MgCl₂ or NaCl. The formation of higher quantity of calcium chloroaluminate in the concrete mixes admixed with CaCl₂ in comparison to MgCl₂, and NaCl is corroborated from the XRD patterns shown in Fig. 4.1, and Fig. 4.2, wherein the peak intensity of calcium chloroaluminate (Friedel's salt) as indicated by its peaks at 11.2° 2θ was higher in case of CaCl₂ in comparison to that in case of MgCl₂, and NaCl for both OPC, and PPC.

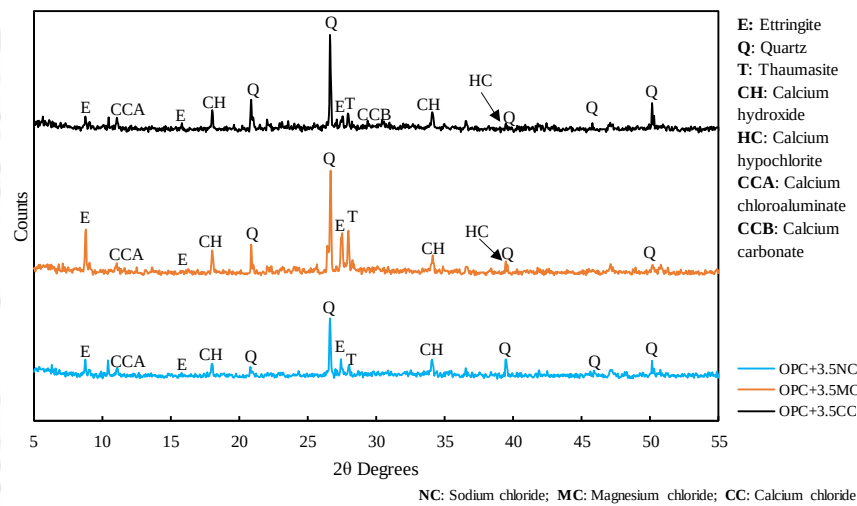


Fig. 4.1 XRD patterns of concrete prepared with OPC, and admixed with different chloride salts

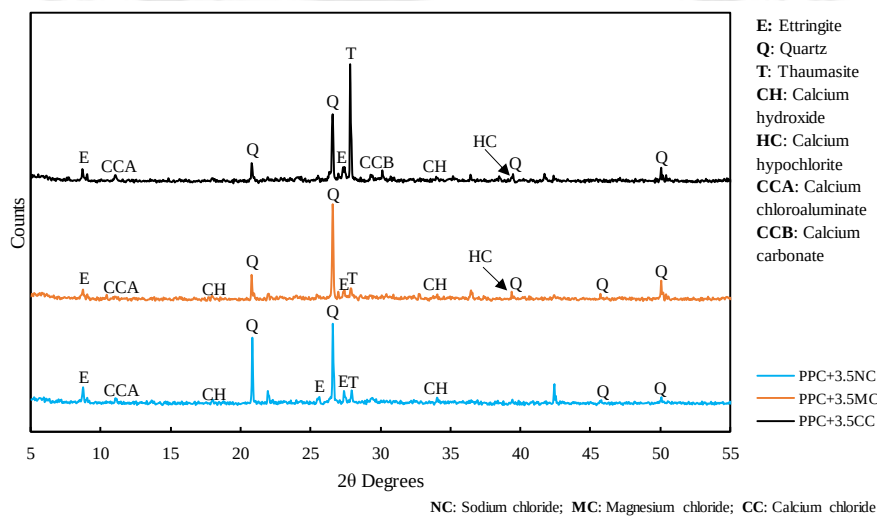


Fig. 4.2 XRD patterns of concrete prepared with PPC, and admixed with different chloride salts

4.2.2 Influence of corrosion inhibitor on compressive strength of concrete

From the average compressive strength, and standard deviation values, it is inferred that the concrete mixes admixed with corrosion inhibitors showed lower compressive strength than control mix irrespective of type of cement, and corrosion inhibitor, as evident from Table 4.1. The lower compressive strength of sodium nitrite (NaNO_2 , SN) admixed concrete mix may be attributed to the retarding effect of NaNO_2 on strength development of concrete [92, 118, 168]. In the concrete mixes admixed with di-Sodium hydrogen phosphate (Na_2HPO_4 , DHP), the reduction in compressive strength in comparison to control concrete may be attributed to the fact that the reaction of phosphates with cement compounds results in the formation of water, and new phosphate products such as acidic hydrated pyrophosphate ($\text{Ca}_3\text{H}_2(\text{P}_2\text{O}_7)_2 \cdot \text{H}_2\text{O}$), and brushite (dicalcium phosphate dihydrate: $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) that results in the disappearance of cement hydrates responsible for strength development of concrete [131]. Although these phosphate compounds block the pores [131] in concrete, the dominant effect of formation of water, and disappearance of cement hydrates results in the reduction of compressive strength of concrete admixed with DHP. The formation of hydrated pyrophosphate, and brushite in the concrete admixed with DHP is corroborated from the XRD patterns shown in Fig. 4.3, and Fig. 4.4, where the peaks of hydrated pyrophosphate were identified at $28.4^\circ 2\theta$, and that of brushite were identified at $11.65^\circ 2\theta$, $20.94^\circ 2\theta$, and $29.25^\circ 2\theta$ for both OPC, and PPC. While comparing the effect of corrosion inhibitors, it is observed that the concrete admixed with NaNO_2 exhibited higher compressive strength than that admixed with DHP for both cements.

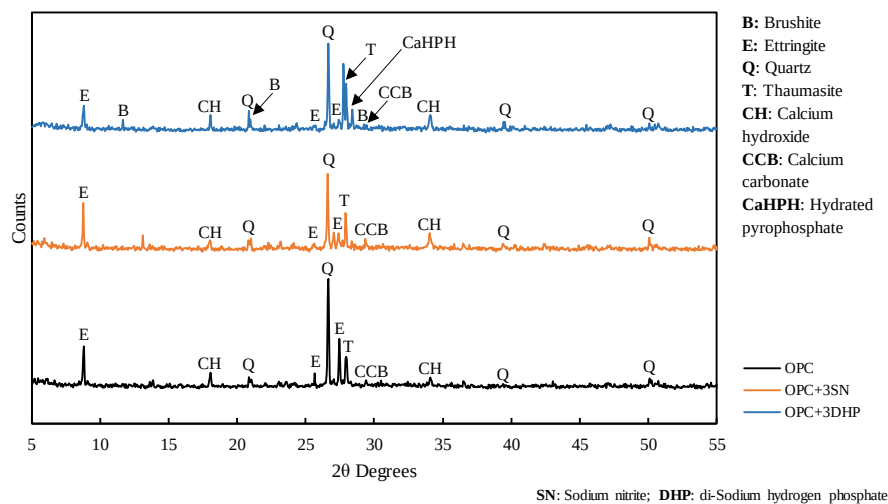


Fig. 4.3 XRD patterns of concrete prepared with OPC, and admixed with or without corrosion inhibitors

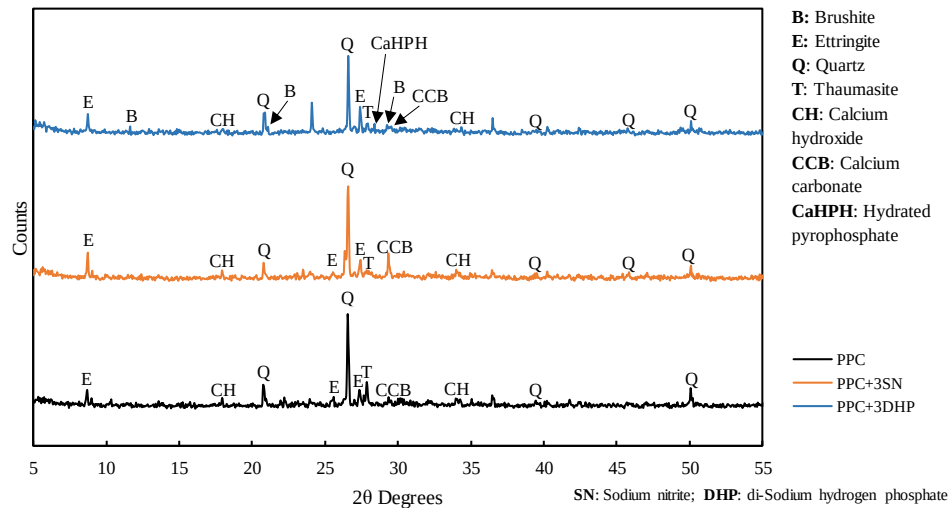


Fig. 4.4 XRD patterns of concrete prepared with PPC, and admixed with or without corrosion inhibitors

4.2.3 Combined effect of chloride salt, and corrosion inhibitor on compressive strength of concrete

From the results shown in Table 4.1, it is inferred that for OPC, the concrete admixed with NaCl, or MgCl₂ plus NaNO₂ mostly showed lower compressive strength than the control mix. This may be due to the dominant effect of NaNO₂ in retarding the strength development of concrete over the accelerating effect of NaCl or MgCl₂. However, OPC concrete admixed with CaCl₂ plus NaNO₂ showed higher compressive strength than the control mix, which may be due to the dominant effect of CaCl₂ in accelerating the strength development of concrete over the retarding effect of NaNO₂. In case of PPC, the concrete mixes admixed with NaCl, MgCl₂, or CaCl₂ plus NaNO₂ exhibited higher compressive strength in comparison to the control mix, as evident from Table 4.1. This is attributed to the dominant effect of the chloride salts in accelerating the hydration, and pozzolanic reactions in PPC concrete. The consumption of calcium hydroxide (CH: portlandite) in the pozzolanic reaction is corroborated from the XRD patterns shown in Fig. 4.5, and Fig. 4.6, where the peak intensity of calcium hydroxide is lower in PPC concrete than that in OPC concrete. The peaks of calcium hydroxide in OPC concrete were observed at 18.1° 2θ, 34.1° 2θ, and 47.2° 2θ with clearly defined peaks at 18.1° 2θ, and 34.1° 2θ. In PPC concrete, the calcium hydroxide peaks were identified at 18.1° 2θ, and 34.1° 2θ with lower intensity in comparison to OPC concrete, as observed from Fig. 4.5, and Fig. 4.6. From Table 4.1, it is observed that for both OPC, and PPC, the concrete mixes admixed with NaCl, MgCl₂ or CaCl₂ plus di-Sodium hydrogen phosphate (DHP) exhibited lower compressive strength

than the control mix except in case of PPC concrete admixed with CaCl_2 plus DHP. The lower compressive strength of concrete admixed with chloride salts, and DHP may be due to the dominant effect of formation of water, and phosphate products such as acidic hydrated pyrophosphate, and brushite in concrete in the presence of DHP, which result in the disappearance of cement hydrates responsible for strength development of concrete. The formation of hydrated pyrophosphate, and brushite in concrete admixed with DHP is substantiated from the XRD patterns shown in Fig. 4.7, and Fig. 4.8, where the peaks of hydrated pyrophosphate were identified at $28.4^\circ 2\theta$, and that of brushite were identified at $20.94^\circ 2\theta$ for both OPC, and PPC. The higher compressive strength of concrete admixed with CaCl_2 , and DHP as compared to the control mix in case of PPC is due to the dominant effect of CaCl_2 in accelerating the hydration, and pozzolanic reactions over the strength reduction effect of DHP. While comparing the effect of chloride salts in the conjoint presence of these salts, and corrosion inhibitors, it is inferred that the concrete admixed with CaCl_2 exhibited higher compressive strength in comparison to MgCl_2 followed by NaCl for both types of cement, and corrosion inhibitor as observed from Table 4.1. Similarly, the concrete mix admixed with NaNO_2 exhibited higher compressive strength than that admixed with DHP for both types of cement, and all chloride salts.

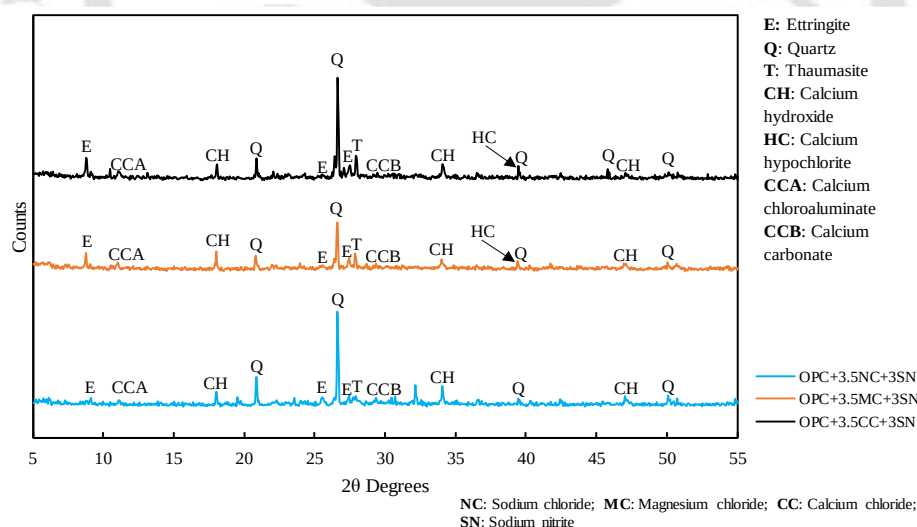


Fig. 4.5 XRD patterns of concrete prepared with OPC, and admixed with different chloride salts, and sodium nitrite

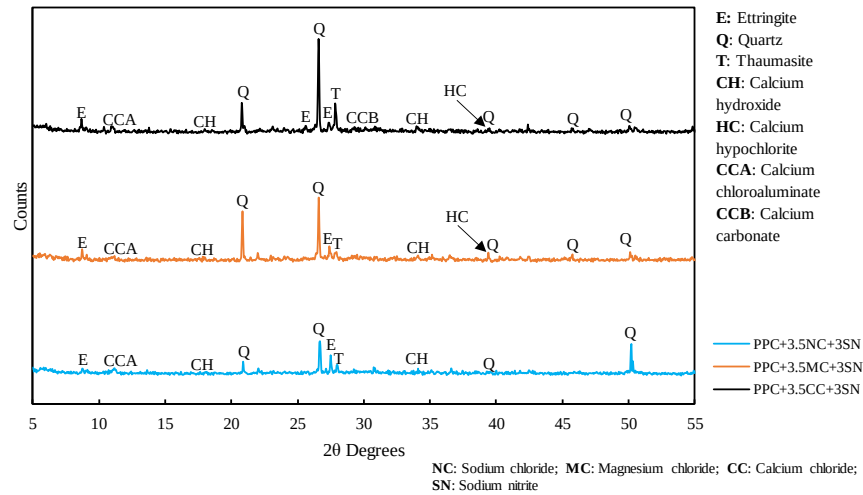


Fig. 4.6 XRD patterns of concrete prepared with PPC, and admixed with different chloride salts, and sodium nitrite

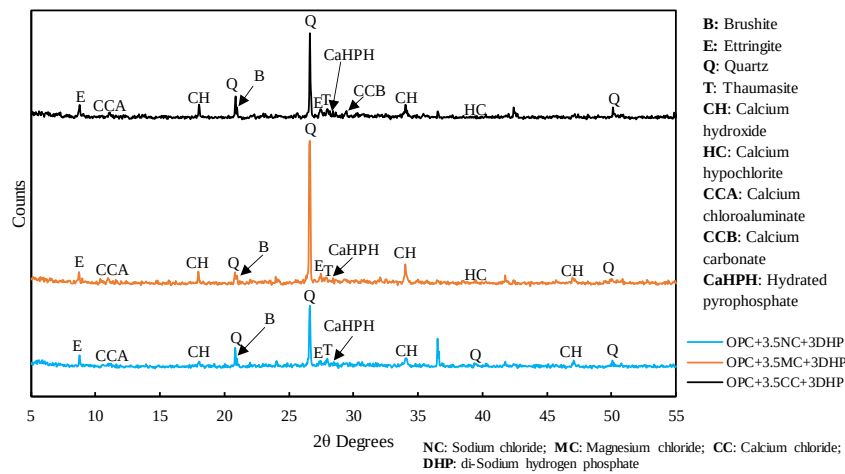


Fig. 4.7 XRD patterns of concrete prepared with OPC, and admixed with different chloride salts, and di-Sodium hydrogen phosphate

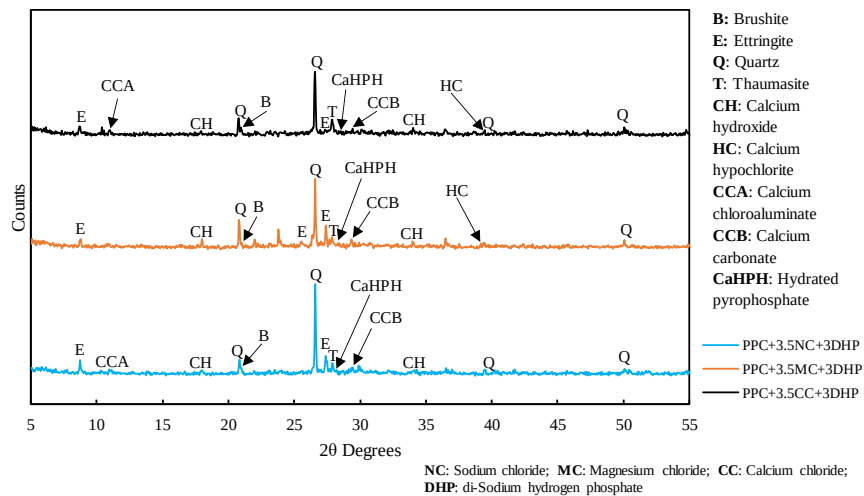


Fig. 4.8 XRD patterns of concrete prepared with PPC, and admixed with different chloride salts, and di-Sodium hydrogen phosphate

4.3 Potentiodynamic polarization measurement

A typical anodic polarization curve obtained from potentiodynamic polarization test on steel reinforcement in concrete powder electrolyte solution (CPES) of control mix prepared from OPC is presented in Fig. 4.9. In this curve, various zones of corrosion such as active zone, passive zone, and transpassivity zone are illustrated. The zone above the equilibrium potential is named as active zone or quasi-immune zone [14, 169]. In this zone, the passive film does not form spontaneously. Because of the proximity to the equilibrium condition, the rate of anodic process in this zone is negligible, and is characterized by low corrosion rate. The zone that lies above the active zone is named as passive zone. In passive zone, the steel surface is covered with passive film (a very thin layer of iron oxide), leading to a very low value of anodic current [14]. In this zone, the increase in potential is significant with a very less variation in current density. Both the active zone, and passive zone can be considered as the zones of negligible corrosion rate [14]. The zone that lies above passive zone is named as transpassivity zone. In this zone, the steel is in the state of transpassivity where oxygen may be produced on the surface of steel in accordance with the anodic reaction of oxygen evolution: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ [14]. This reaction produces acidity, and sufficient quantity of acidity can neutralize the concrete alkalinity that leads to the breakdown of passive film over the steel, and can initiate the process of corrosion [14]. When chloride ions are present, the transpassivity zone is named as pitting zone [14, 169]. The equilibrium potential, act/pass zone boundary potential (i.e., potential at the point of change from active to passive state), and pass/transpass zone boundary potential (i.e., potential at the point of change from passive state to transpassive state) are shown in the anodic polarization curve (Fig. 4.9). In the presence of chloride ions, the pass/pitt zone boundary potential is known as pitting potential or breakdown potential. Anodic polarization curve of steel reinforcement in concrete powder electrolyte solution (CPES) of control mix prepared from PPC is presented in Fig. 4.10. Furthermore, anodic polarization curves of reinforcing steel in concrete powder electrolyte solution (CPES) prepared from concrete mixes admixed with only corrosion inhibitors, only chloride salts, and those admixed with chloride salts, and corrosion inhibitors are shown in Fig. 4.11 to Fig. 4.18 for OPC, and PPC.

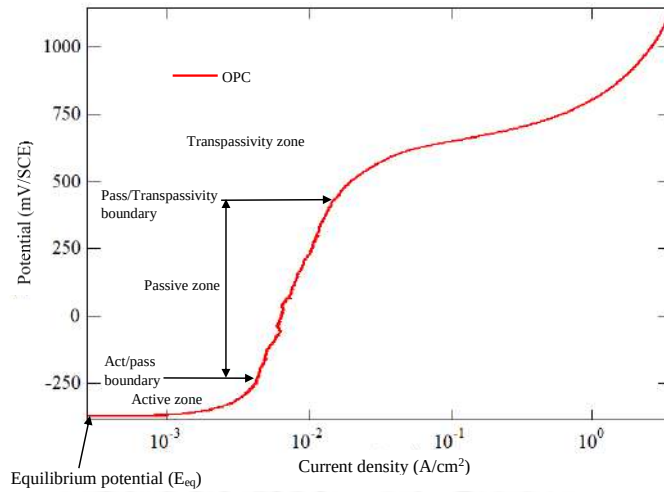


Fig. 4.9 Anodic polarization curve of reinforcing steel in OPC based CPES prepared from control mix

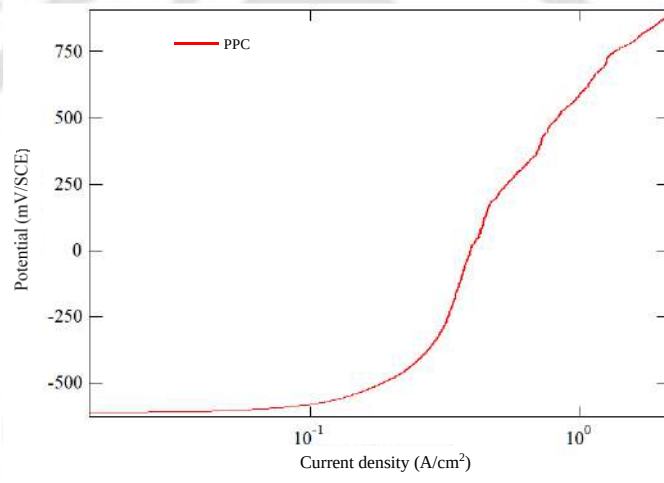
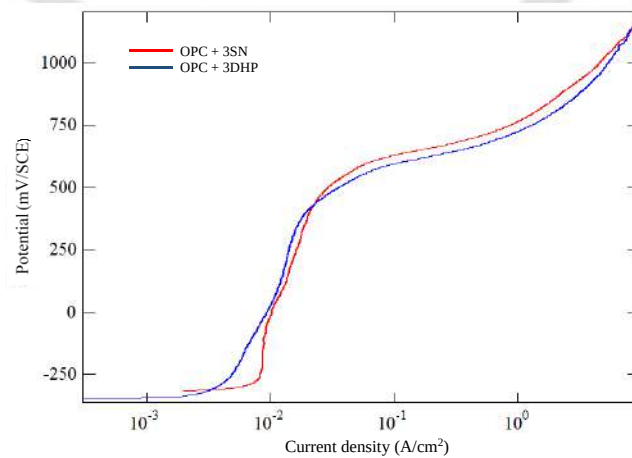


Fig. 4.10 Anodic polarization curve of reinforcing steel in PPC based CPES prepared from control mix



SN: Sodium nitrite; DHP: di-Sodium hydrogen phosphate

Fig. 4.11 Anodic polarization curves of reinforcing steel in OPC based CPES admixed with different corrosion inhibitors

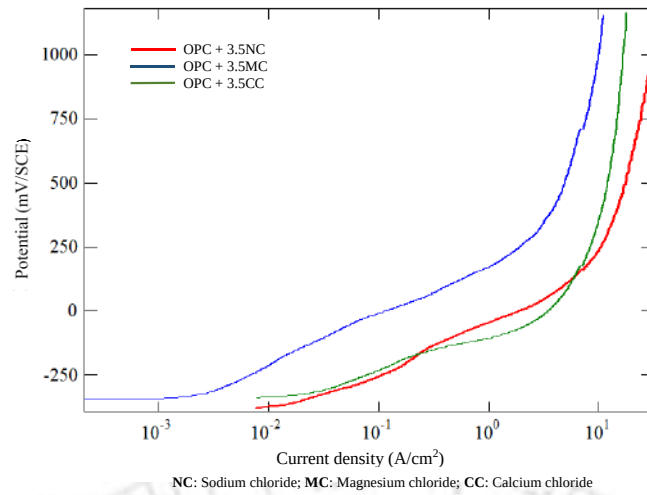


Fig. 4.12 Anodic polarization curves of reinforcing steel in OPC based CPES admixed with different chloride salts

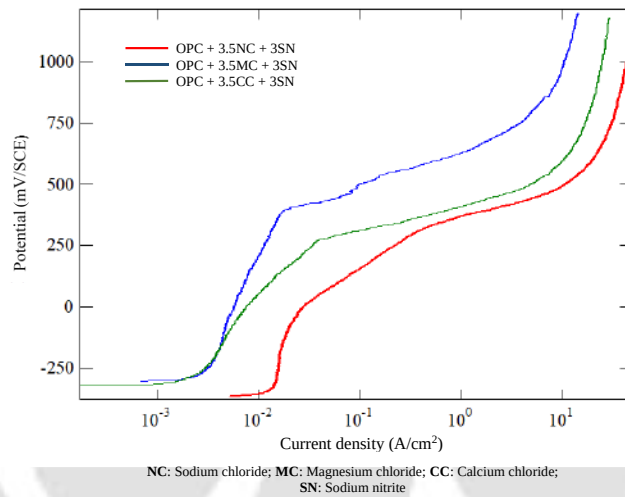


Fig. 4.13 Anodic polarization curves of reinforcing steel in OPC based CPES admixed with different chloride salts, and sodium nitrite

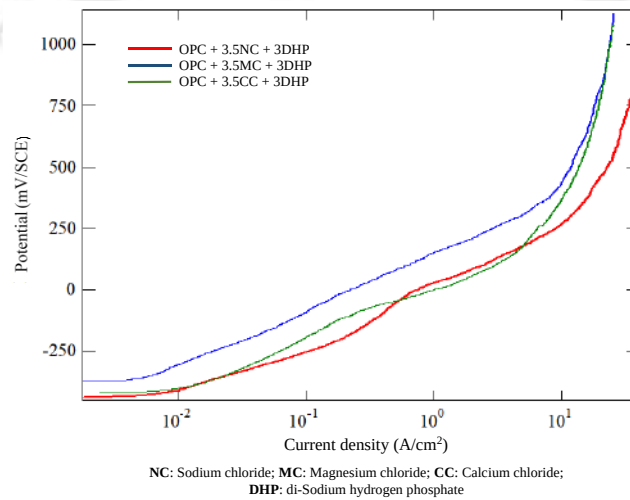


Fig. 4.14 Anodic polarization curves of reinforcing steel in OPC based CPES admixed with different chloride salts, and di-Sodium hydrogen phosphate

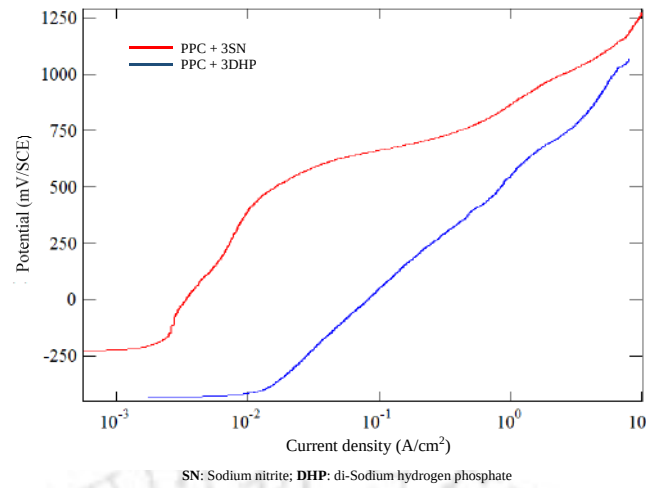


Fig. 4.15 Anodic polarization curves of reinforcing steel in PPC based CPES admixed with different corrosion inhibitors

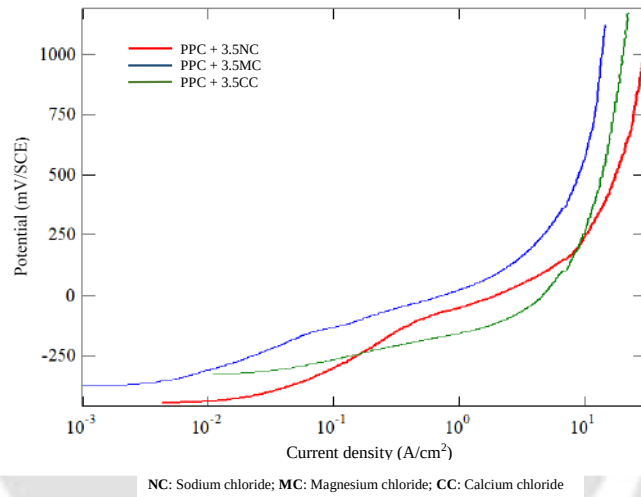


Fig. 4.16 Anodic polarization curves of reinforcing steel in PPC based CPES admixed with different chloride salts

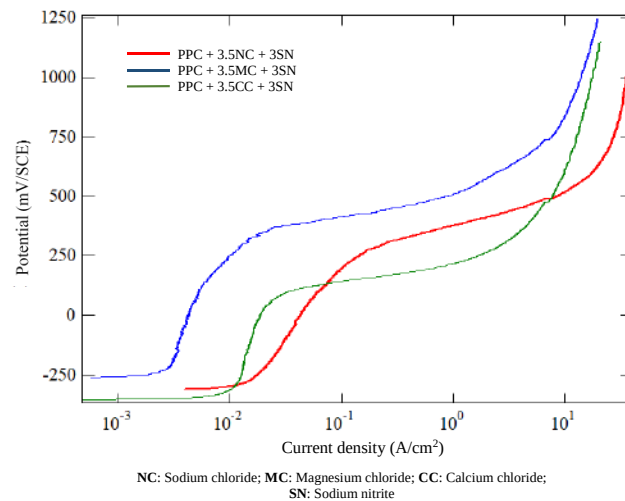


Fig. 4.17 Anodic polarization curves of reinforcing steel in PPC based CPES admixed with different chloride salts, and sodium nitrite

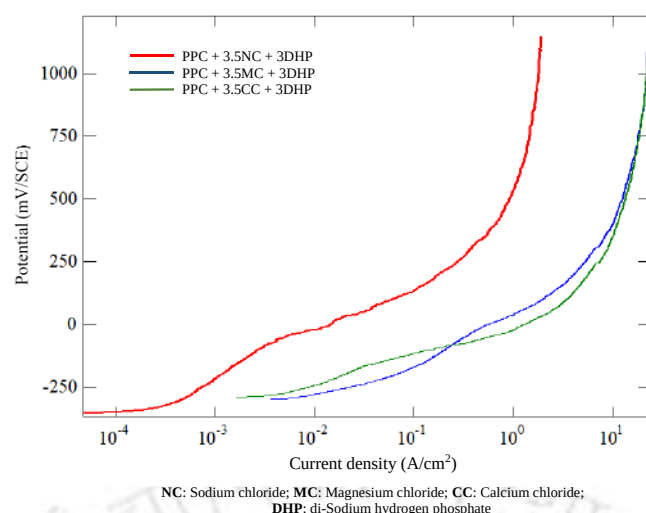


Fig. 4.18 Anodic polarization curves of reinforcing steel in PPC based CPES admixed with different chloride salts, and di-Sodium hydrogen phosphate

From all the experimentally obtained polarization curves, equilibrium potential, act/pass zone boundary potential, and pass/pitt zone boundary potential values were determined, and are shown in Table 4.2. In addition, in Table 4.2, the passivity range, which is calculated as the difference between pass/pitt zone boundary potential, and act/pass zone boundary potential is also mentioned. From Table 4.2, it is inferred that that the range of passive zone (passivity range) is higher in the CPES prepared from control mix, and that admixed with only corrosion inhibitors in comparison to the CPES admixed with chloride salts (irrespective of cation type of chloride salts), and that admixed with chloride salts, and corrosion inhibitors.

Table 4.2 Equilibrium potential, and boundary potential values of reinforcing steel in OPC, and PPC based concrete powder electrolyte solution (CPES)

Cement type	Admixed chloride salt concentration	Admixed corrosion inhibitor concentration	Equilibrium potential (mV/SCE)	Act/pass zone boundary potential (mV/SCE)	Pass/pitt zone boundary potential* (pitting potential) (mV/SCE)	Passivity range (mV/SCE)
OPC	0%	0% (Control)	-372.56	-235.03	450.81	685.84
		3% NaNO ₂	-314.61	-263.60	415.37	678.97
		3% DHP	-347.06	-256.21	376.80	633.01
	3.5% NaCl	0%	-376.87	-197.10	-158.52	38.58
		3% NaNO ₂	-362.85	-322.00	-33.12	288.88
		3% DHP	-436.21	-159.90	-16.80	143.10
	3.5% MgCl ₂	0%	-345.50	-248.54	-181.58	66.96
		3% NaNO ₂	-303.59	-209.73	36.256	245.99
		3% DHP	-376.18	-341.82	-236.38	105.44
	3.5% CaCl ₂	0%	-337.70	-274.20	-178.32	95.88
		3% NaNO ₂	-322.26	-236.30	7.693	243.99
		3% DHP	-422.93	-243.38	-123.30	120.08
PPC	0%	0% (Control)	-546.0	-398.15	148.77	546.92
		3% NaNO ₂	-224.22	-154.39	394.79	549.18
		3% DHP	-431.88	-405.03	-191.30	213.73
	3.5% NaCl	0%	-444.27	-127.80	-105.16	22.64
		3% NaNO ₂	-310.35	-223.16	49.67	272.83
		3% DHP	-351.93	-218.29	-111.39	106.90
	3.5% MgCl ₂	0%	-377.50	-300.20	-245.18	55.02
		3% NaNO ₂	-258.73	-186.08	45.89	231.97
		3% DHP	-297.44	-248.55	-170.54	78.01
	3.5% CaCl ₂	0%	-327.75	-269.47	-205.54	63.93
		3% NaNO ₂	-351.20	-240.31	1.77	242.08
		3% DHP	-289.93	-239.59	-159.41	80.18

* Pass/transpass zone boundary potential for steel reinforcement in CPES without any chloride salt.

4.3.1 Influence of chloride salts on passivity of reinforcing steel

From Table 4.2, it is inferred that the equilibrium potential of steel is less negative in the concrete powder electrolyte solution (CPES) admixed with CaCl₂ than that admixed with MgCl₂ followed by NaCl for both OPC, and PPC. While analyzing the passivity of steel, it is observed that the range of passive zone of steel is higher in the CPES admixed with CaCl₂

than that admixed with MgCl_2 , and NaCl . This indicates that CaCl_2 maintains the passivity of steel reinforcement comparatively to a greater degree than MgCl_2 , and NaCl . The lower range of passivity of steel in case of MgCl_2 as compared to CaCl_2 may be attributed to the formation of higher amount of calcium hypochlorite in the presence of MgCl_2 that results in lowering of alkalinity of concrete due to consumption of calcium hydroxide (CH). The lower alkalinity of concrete powder electrolyte solution admixed with MgCl_2 is corroborated from the lower pH value shown in Table 4.1, as compared to that admixed with CaCl_2 . The reaction of MgCl_2 with calcium hydroxide (CH) forms Mg(OH)_2 , and CaCl_2 . The CaCl_2 thus formed further reacts with calcium hydroxide in the presence water to form calcium hypochlorite [52]. The formation of calcium hypochlorite (HC) is indicated by its peaks at $39.4^\circ 2\theta$ in the XRD patterns shown in Figs. 4.1, and 4.2 for OPC, and PPC respectively, in the concrete mixes admixed with CaCl_2 , and MgCl_2 . The peak intensity of calcium hypochlorite was higher in the concrete admixed with MgCl_2 than that admixed with CaCl_2 as observed from the XRD patterns. Further, in the presence of MgCl_2 , the attack of Mg^{2+} ions on C-S-H converts it to non-cementitious magnesium silicate hydrate (M-S-H). Thus, the reduced alkalinity in the presence of MgCl_2 is responsible for lower range of passivity of steel reinforcement in comparison to CaCl_2 [52]. From the free chloride ion (C_F) content shown in Fig. 4.19 (for OPC), and Fig. 4.20 (for PPC), it is observed that among the three chloride salts, the trend of free chloride ion content is C_F : $\text{NaCl} > C_F$: $\text{CaCl}_2 > C_F$: MgCl_2 , for both OPC, and PPC. The lower free chloride ion content in the concrete admixed with MgCl_2 in comparison to that in the concrete admixed with CaCl_2 may be attributed to the formation of higher amount of calcium hypochlorite in the concrete admixed with MgCl_2 . Thus, lower alkalinity in case of MgCl_2 was more dominant in decreasing the passivity of reinforcing steel over the higher free chloride ion content in case of CaCl_2 . Further, the trend of bound chloride ion content (shown in Fig. 4.19, and Fig. 4.20) is C_B : $\text{CaCl}_2 > C_B$: $\text{MgCl}_2 > C_B$: NaCl , for both OPC, and PPC. The higher bound chloride ion (C_B) content in the concrete admixed with CaCl_2 as compared to MgCl_2 is due to more chloride binding with C-S-H in the concrete admixed with CaCl_2 in comparison to lower chloride binding with M-S-H formed in the concrete admixed with MgCl_2 . The lower range of passivity of reinforcing steel in the CPES admixed with NaCl than that admixed with CaCl_2 may be due to higher free chloride ion content in case of NaCl in comparison to CaCl_2 , as observed from Fig. 4.19, and Fig. 4.20. The higher free chloride ion content in the concrete admixed with NaCl may be attributed to the increased solubility of Friedel's salt due to increase in pH value of concrete in the presence of Na^+ ion, thus leading to

release of bound chloride [52]. It is to be noted that the pH value of concrete admixed with NaCl was higher than that admixed with CaCl_2 , as observed from Table 4.1. The higher free chloride ion content in case of NaCl was more dominant in decreasing the passivity of reinforcing steel over the lower pH value in case of CaCl_2 . Further, the higher bound chloride ion content in case of CaCl_2 in comparison to NaCl (Fig. 4.19, and Fig. 4.20) is substantiated by the formation of higher amount of calcium chloroaluminate (CCA) as indicated by its peaks at $11.2^\circ 2\theta$ in the XRD patterns shown in Fig. 4.1, and Fig. 4.2 for OPC, and PPC respectively. The peak intensity of calcium chloroaluminate was higher in the concrete admixed with CaCl_2 than that admixed with NaCl. While analyzing the pitting potential, it is inferred that the pitting potential was more negative in the CPES admixed with chloride salts (irrespective of cation type associated with chloride ion) than that prepared from control mix for both types of cement as evident from Table 4.2. Further, the pitting potential of reinforcing steel was more negative in the CPES admixed with MgCl_2 than those admixed with CaCl_2 , and NaCl.

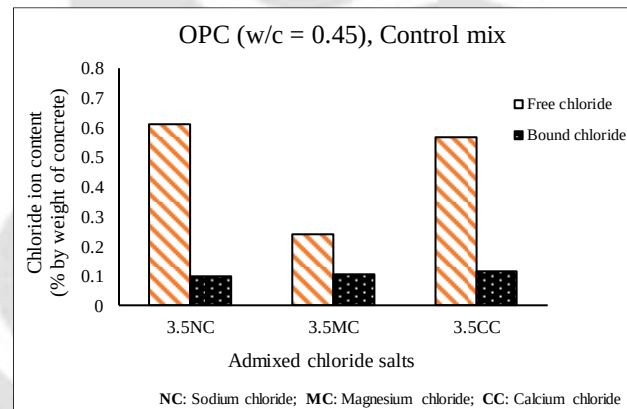


Fig. 4.19 Free, and bound chloride ion contents of OPC concrete admixed with different chloride salts

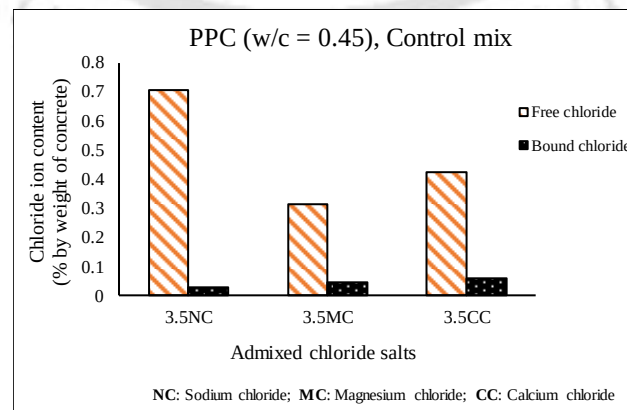
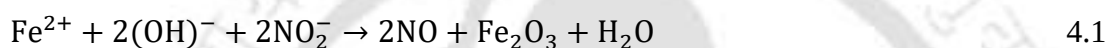


Fig. 4.20 Free, and bound chloride ion contents of PPC concrete admixed with different chloride salts

4.3.2 Influence of corrosion inhibitors on passivity of reinforcing steel in the presence of chloride ions

From the boundary potential values shown in Table 4.2, it is inferred that the passivity range of reinforcing steel increased due to the addition of corrosion inhibitors in chloride contaminated concrete irrespective of type of chloride salt, and cement type, in comparison to the passivity range of steel in the concrete admixed with only chloride salts. This indicates that the addition of corrosion inhibitors in chloride contaminated concrete enhanced the passivity of reinforcing steel. The higher passivity range in the presence of sodium nitrite (NaNO_2) may be due to the fact that the nitrite ions compete with chloride ions to react with ferrous ions to form ferric oxide that passivates the reinforcing steel [85]. The reaction is shown below [85].



The above reaction is faster than corrosion reaction [18]. Thus, the presence of nitrite ions results in the formation of passive layer on surface of steel reinforcement even in the presence of chloride ions [18]. Further, it is observed that the pH value of concrete powder electrolyte solution (CPES) increased due to the addition of NaNO_2 in the chloride contaminated concrete mixes irrespective of chloride salt, and cement type in comparison to the CPES admixed with only chloride salts as evident from Table 4.1. While evaluating the effect of NaNO_2 on passivity of reinforcing steel among chloride salts, it is observed that the NaNO_2 is more effective in enhancing the passivity of steel reinforcement in concrete admixed with NaCl in comparison to CaCl_2 , and MgCl_2 for both types of cement, as the range of passive zone is higher in NaCl than that in CaCl_2 , and MgCl_2 . The better performance of NaNO_2 in the presence of NaCl may be attributed to the repelling of negatively charged chloride ions from steel surface by negatively charged nitrite ions [76] to a greater degree, thereby enhancing the passivity of reinforcing steel. Further, the pH value of CPES admixed with NaCl was higher than those admixed with CaCl_2 , and MgCl_2 in the presence of NaNO_2 . The higher passivity range of steel reinforcement in chloride contaminated concrete due to addition of di-Sodium hydrogen phosphate (DHP) in comparison to only chloride contaminated concrete may be attributed to the protective action of phosphate compounds such as strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) or iron phosphate (FePO_4), which are formed as a result of reaction of phosphate ions with iron (III) ions. The reactions are shown below [83].



The protective action is due to the formation of passive layer of these compounds on the surface of steel. The chemical stability of these compounds reduces the formation of corrosion products such as FeCl_3 , thereby enhancing the passivity of reinforcing steel in the presence of DHP. Further, the addition of DHP in chloride admixed concrete increased its pH value as compared to the concrete admixed with only chloride salts as observed from Table 4.1. On analyzing the effect of DHP on passivity of reinforcing steel among chloride salts, it is inferred that the passivity range is higher in the concrete admixed with NaCl than those admixed with CaCl_2 , and MgCl_2 in both OPC, and PPC. This indicates that DHP is more effective in enhancing the passivity of steel in the presence of chloride ions associated with Na^+ cation as compared to that associated with Ca^{2+} or Mg^{2+} cation. The improved performance of DHP (di-Sodium hydrogen phosphate) in enhancing the passivity of reinforcing steel in the presence of chloride ions associated with Na^+ cation as compared to that associated with Ca^{2+} or Mg^{2+} cation may be attributed to the effect of higher pH value of electrolyte concrete powder solution admixed with NaCl as observed from Table 4.1. The higher pH value favours the formation of a comparatively more stable passive film on steel surface [102]. Further, the pitting potential of reinforcing steel was less negative in the CPES admixed with corrosion inhibitors, and chloride salts than that in the CPES admixed with only chloride salts as observed from Table 4.2. While comparing the effect of type of corrosion inhibitor, it is inferred that the passivity range of steel reinforcement is higher in the presence of NaNO_2 than that in the presence of DHP in the chloride contaminated concrete for both types of cement, although the CPES admixed with DHP showed higher pH value in comparison to that admixed with NaNO_2 . The higher passivity range in case of NaNO_2 may be due to the dominant effect of the ability of nitrite ions to repel the chloride ions from the surface of steel [170] to a greater extent than the phosphate ions, as compared to the effect of higher pH value in case of DHP. Further, as reported in the literature [102], DHP (di-Sodium hydrogen phosphate) is a non-oxidizing inhibitor, and is effective in the presence of oxygen whereas sodium nitrite is an oxidizing inhibitor. The dissolved oxygen level in the concrete powder electrolyte solution (CPES) might be less due to boiling, which resulted in inferior performance of di-Sodium hydrogen phosphate as compared to sodium nitrite as nitrite ions do not require oxygen for stable passive film. In the concrete mixes admixed with chloride salts, and corrosion inhibitors, the trends of both

free chloride ion, and bound chloride ion contents among the three chloride salts were same as that in the concrete added with only chloride salts as observed from Fig. 4.21 to Fig. 4.24 for both types of cement, and corrosion inhibitors. This indicates that the presence of inhibitors did not affect the variations in chloride ion content of concrete among the chloride salts.

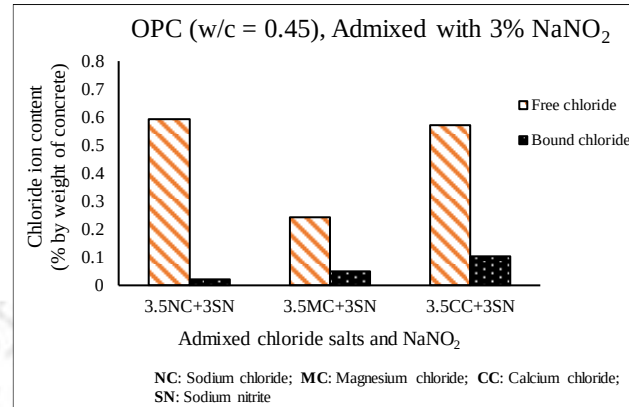


Fig. 4.21 Free, and bound chloride ion contents of OPC concrete admixed with different chloride salts, and sodium nitrite

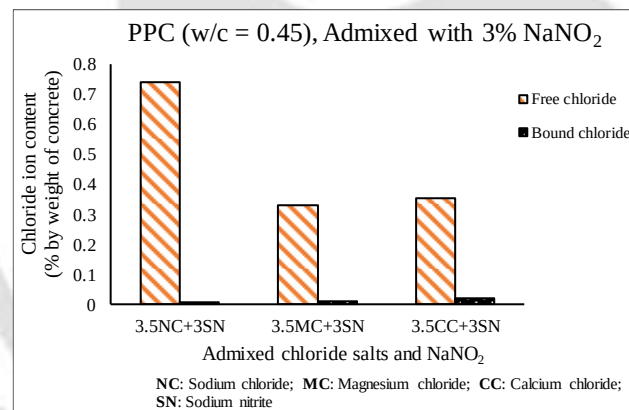


Fig. 4.22 Free, and bound chloride ion contents of PPC concrete admixed with different chloride salts, and sodium nitrite

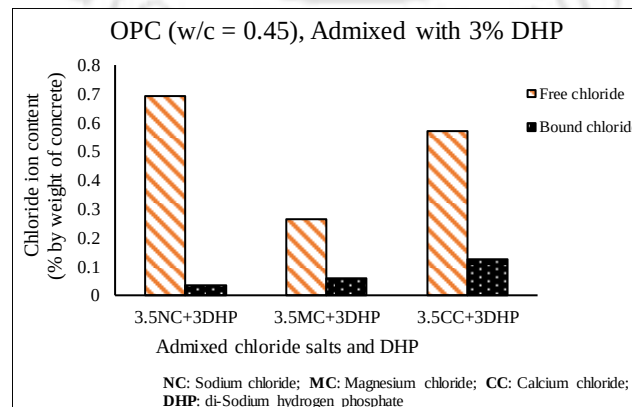


Fig. 4.23 Free, and bound chloride ion contents of OPC concrete admixed with different chloride salts, and di-Sodium hydrogen phosphate

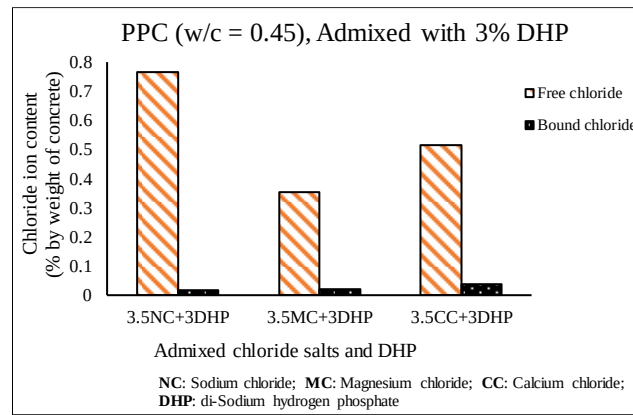


Fig. 4.24 Free, and bound chloride ion contents of PPC concrete admixed with different chloride salts, and di-Sodium hydrogen phosphate

4.3.3 Influence of cement type on passivity of reinforcing steel

From the boundary potential values presented in Table 4.2, it is observed that the passivity range of reinforcing steel in the CPES prepared from OPC is higher than that prepared from PPC for all chloride salts, and both corrosion inhibitors. This may be due to higher alkalinity, and higher chloride binding in OPC concrete than that in PPC concrete. As observed from Table 4.1, the pH value was higher in OPC concrete than that in PPC concrete irrespective of chloride salt, and corrosion inhibitor. The higher alkalinity in OPC concrete is due to the presence of more amount of calcium hydroxide (CH), in comparison to that in PPC concrete, which is indicated by more intense peaks of calcium hydroxide in OPC concrete than that in PPC concrete, as observed from the XRD patterns shown in Fig. 4.1 to Fig. 4.8. The higher chloride binding in OPC concrete was indicated by more bound chloride ion content than that in PPC concrete for all chloride salts, and corrosion inhibitors as observed from Fig. 4.19 to Fig. 4.24. The more chloride binding in OPC concrete in comparison to that in PPC concrete is also corroborated from the XRD patterns shown in Fig. 4.1, Fig. 4.2, and Fig. 4.5 to Fig. 4.8, where calcium chloroaluminate (CCA) peaks were more intense in OPC concrete than that in PPC concrete. The formation of more amount of calcium chloroaluminate in OPC concrete is due to the reaction of hydrated C_3A with chloride ions to a greater extent because of higher C_3A content in OPC than that in PPC. In the XRD patterns shown in Fig. 4.1 to Fig. 4.8, the ettringite (E) peaks were found at $8.8^\circ 2\theta$, $25.6^\circ 2\theta$, and $27.5^\circ 2\theta$. The presence of ettringite in concrete is attributed to its formation due to the reaction between gypsum, and C_3A of cement. The presence of gypsum is due to its addition to the cement clinker during the process of manufacturing to control the early setting, and hardening behaviour of Portland cement. Further, the peaks for quartz were found at $20.78^\circ 2\theta$, $26.65^\circ 2\theta$, $39.45^\circ 2\theta$, and $50.2^\circ 2\theta$ in both OPC, and

PPC concrete. The presence of quartz is mainly because of the aggregates present in concrete. The peaks of calcium carbonate (CaCO_3 : CCB) were found at $29.4^\circ 2\theta$. The peaks of thaumasite (T) were observed at $27.9^\circ 2\theta$ for both types of cement. The formation of thaumasite may either be due to the reaction between C-S-H, calcium carbonate (CaCO_3), and calcium sulfate in the presence of water or it may be formed through a woodfordite route as a result of the reaction between C-S-H, calcium carbonate, and ettringite in the presence of water [171].

4.4 Fourier transform infrared (FTIR) spectroscopy

The FTIR spectroscopy was performed to identify the functional groups associated with different compounds present in concrete prepared from OPC, and PPC. The obtained FTIR spectra of concrete mixes in the presence of chloride salts, and corrosion inhibitors are shown in Fig. 4.25 to Fig. 4.28 for OPC, and Fig. 4.29 to Fig. 4.32 for PPC. The broad bands in the range of $3433 - 3452 \text{ cm}^{-1}$, and from $1627 - 1645 \text{ cm}^{-1}$ in OPC concrete, and those in the range of $3437 - 3456 \text{ cm}^{-1}$, and from $1636 - 1642 \text{ cm}^{-1}$ in PPC concrete can be attributed to the stretching, and bending vibrations of O-H band associated with H_2O molecules present in OPC, and PPC concrete mixes [171-176]. The presence of calcium hydroxide (CH) in OPC, and PPC concrete as evident from the XRD peaks at $18.1^\circ 2\theta$, $34.1^\circ 2\theta$, and $47.2^\circ 2\theta$ (Fig. 4.1 to Fig. 4.8) is further substantiated by the peaks in FTIR spectra in the range of $3637 - 3643 \text{ cm}^{-1}$ in OPC concrete, and in the range of $3640 - 3643 \text{ cm}^{-1}$ in PPC concrete, which is caused by the stretching band of O-H group corresponding to calcium hydroxide [171, 177]. Further in OPC concrete, the bands ranging from $1420 - 1426 \text{ cm}^{-1}$, and in PPC concrete, the bands ranging from $1418 - 1426 \text{ cm}^{-1}$ correspond to CO_3^{2-} associated with calcium carbonate [171-175, 177, 178], which substantiates its peak at $29.4^\circ 2\theta$ in the XRD patterns shown in Fig. 4.1 to Fig. 4.8. Similarly, the bands ranging from $874 - 876 \text{ cm}^{-1}$ in OPC concrete, and from $873 - 876 \text{ cm}^{-1}$ in PPC concrete correspond to the out-of-plane bending of CO_3^{2-} bands [172-175, 177, 178]. The XRD patterns (Fig. 4.1 to Fig. 4.8) indicating the presence of ettringite with peaks at $8.8^\circ 2\theta$, and $27.5^\circ 2\theta$ in OPC, and PPC concrete is further corroborated by the FTIR spectra showing Al-O peaks ranging from $776 - 778 \text{ cm}^{-1}$ in OPC concrete, and the peaks at 777 cm^{-1} , and 778 cm^{-1} in PPC concrete [172]. The bands in the range of $1004 - 1007 \text{ cm}^{-1}$ in OPC concrete, and those in the range of $1004 - 1012 \text{ cm}^{-1}$ in PPC concrete are due to the Si-O asymmetric stretching vibration contributed due to the presence of calcium silicate hydrate (C-S-H) [174-176, 179]. Further, the bands in the range of $534 - 539 \text{ cm}^{-1}$ in OPC concrete, and those in the

range of 534 - 539 cm^{-1} in PPC concrete are attributed to the presence of anhydrous calcium silicate [174, 179]. The band at 1270 cm^{-1} in the FTIR spectra shown in Fig. 4.25, Fig. 4.27, Fig. 4.29, and Fig. 4.31 is attributed to the presence of nitrite [105] due to the use of sodium nitrite in concrete. Further, a complex group of bands in the range of 500 - 700 cm^{-1} in the FTIR spectra shown in Fig. 4.25, Fig. 4.28, Fig. 4.29, and Fig. 4.32 may be attributed to the presence of phosphates in concrete due to the use of di-sodium hydrogen phosphate [105].

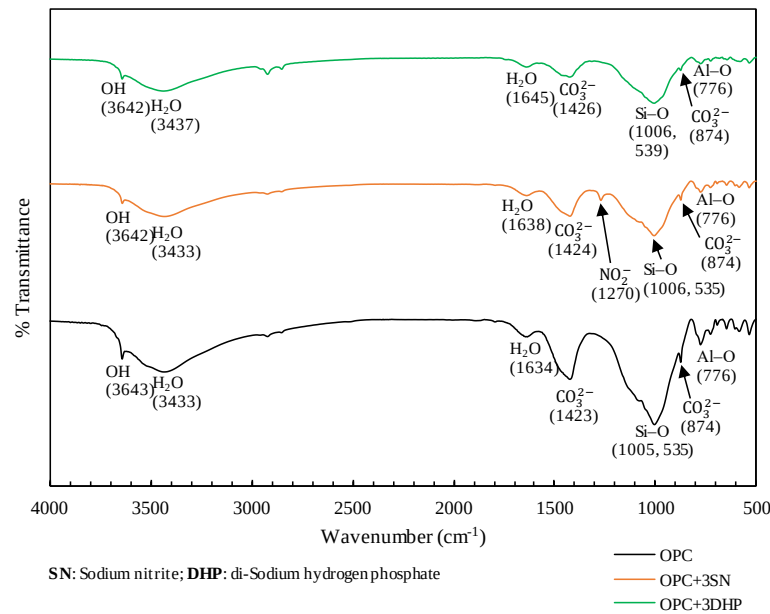


Fig. 4.25 FTIR spectra of concrete prepared with OPC, and admixed with or without corrosion inhibitors

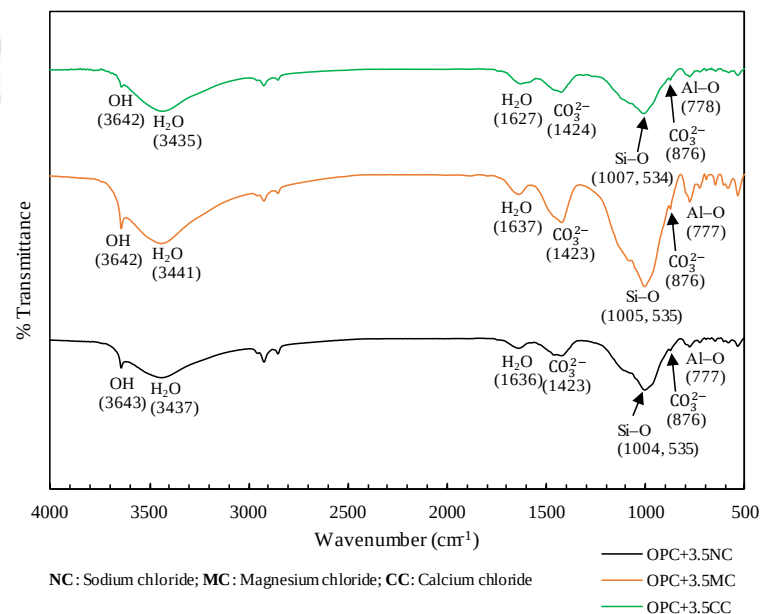


Fig. 4.26 FTIR spectra of concrete prepared with OPC, and admixed with different chloride salts

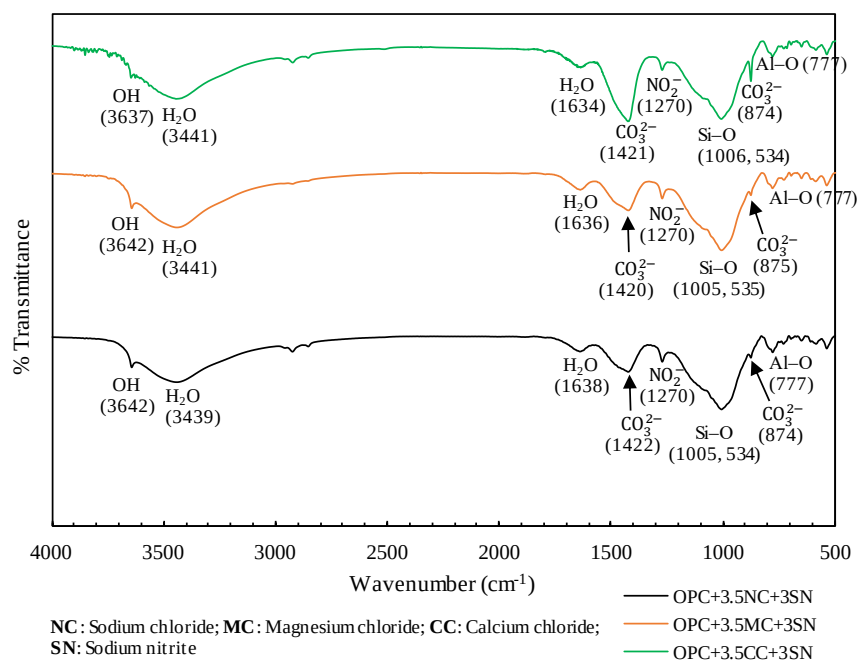


Fig. 4.27 FTIR spectra of concrete prepared with OPC, and admixed with different chloride salts, and sodium nitrite

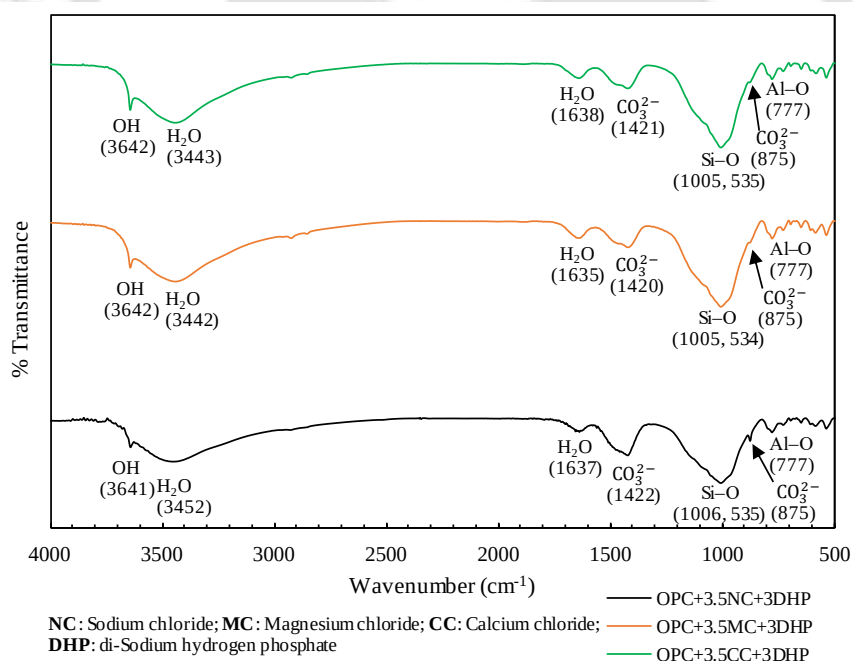


Fig. 4.28 FTIR spectra of concrete prepared with OPC, and admixed with different chloride salts, and di-Sodium hydrogen phosphate

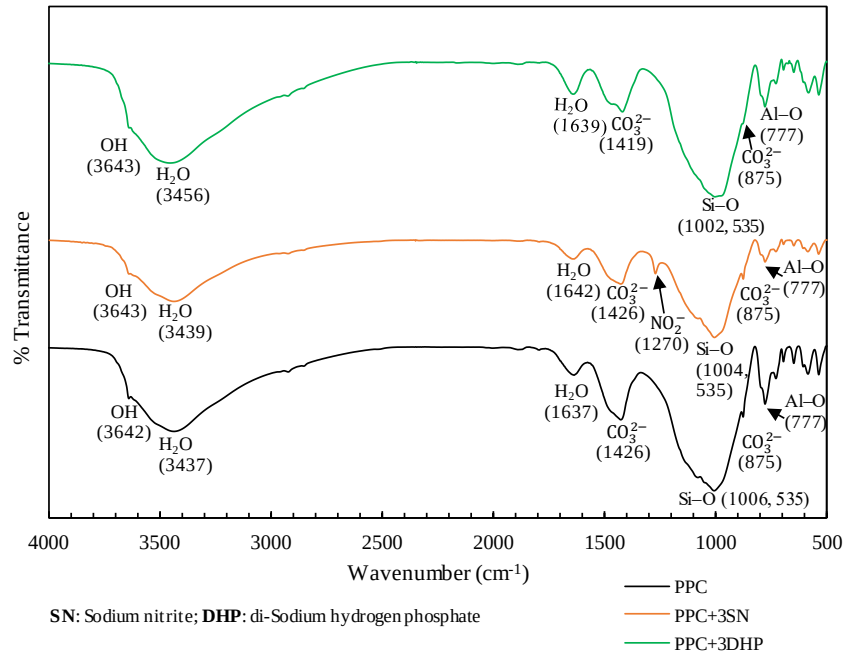


Fig. 4.29 FTIR spectra of concrete prepared with PPC, and admixed with or without corrosion inhibitors

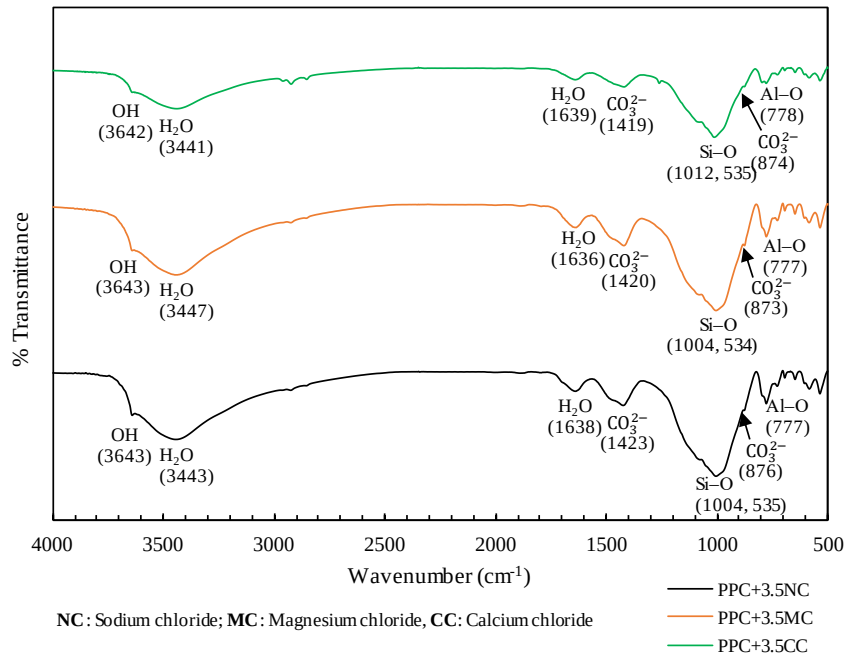


Fig. 4.30 FTIR spectra of concrete prepared with PPC, and admixed with different chloride salts

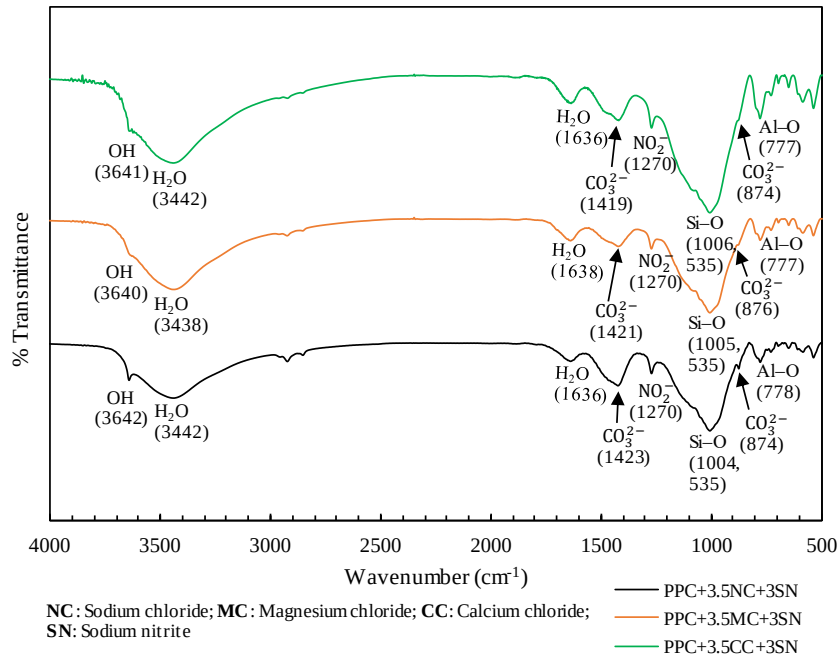


Fig. 4.31 FTIR spectra of concrete prepared with PPC, and admixed with different chloride salts, and sodium nitrite

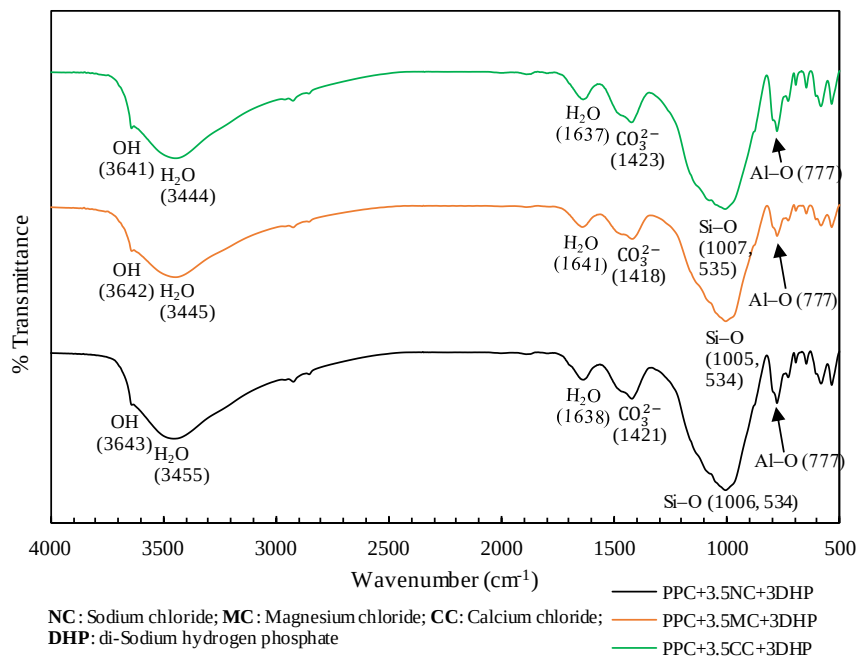


Fig. 4.32 FTIR spectra of concrete prepared with PPC, and admixed with different chloride salts, and di-Sodium hydrogen phosphate

4.5 Summary

The obtained results showed that the addition of different chloride salts increased the compressive strength of concrete as compared to the control mix. Among chloride salts, the concrete admixed with CaCl_2 showed higher compressive strength as compared to that

admixed with MgCl_2 followed by NaCl irrespective of cement type, and corrosion inhibitors. The addition of corrosion inhibitors decreased the compressive strength of concrete as compared to the control mix. The concrete admixed with di-Sodium hydrogen phosphate showed lower compressive strength as compared to that admixed with sodium nitrite irrespective of cement type, and chloride salts. The passivity range of steel reinforcement was higher in the concrete powder electrolyte solution (CPES) admixed with CaCl_2 as compared to MgCl_2 , and NaCl irrespective of cement type whereas, in the presence of corrosion inhibitors, the passivity range of steel reinforcement was higher in the CPES admixed with NaCl as compared to CaCl_2 , and MgCl_2 . The presence of corrosion inhibitors increased the passivity of reinforcing steel in the CPES admixed with chloride salts. Between both corrosion inhibitors, sodium nitrite (NaNO_2) was more effective in enhancing the passivity of reinforcing steel as compared to di-sodium hydrogen phosphate (DHP) in the presence of chloride salts. Between OPC and PPC, the passivity range of steel reinforcement in the CPES was higher in case of OPC as compared to PPC irrespective of chloride salts, and corrosion inhibitors. The results obtained from chloride analysis indicated following trend of free chloride ion (C_F) content, i.e., $C_F: \text{NaCl} > C_F: \text{CaCl}_2 > C_F: \text{MgCl}_2$, and the trend of bound chloride ion (C_B) content was; $C_B: \text{CaCl}_2 > C_B: \text{MgCl}_2 > C_B: \text{NaCl}$ for both types of cement, and corrosion inhibitors. From the microstructure analysis, the formation of various compounds in the concrete in the presence of chloride salts and corrosion inhibitors as indicated by the XRD patterns were substantiated with the FTIR spectra showing the functional groups associated with these compounds formed in concrete.

Effect of Corrosion Inhibitors on Rebar Corrosion in Concrete in the Presence of Internal Chloride

5.1 General

In this chapter, the results obtained from the experimental investigation carried out to evaluate the effect of corrosion inhibitors on corrosion behaviour of steel reinforcement in concrete in the presence of internal chloride are presented and discussed. The concrete mixes were prepared from two types of cement, i.e., OPC and PPC at a w/c of 0.45 and admixed with different chloride salts (i.e., sodium chloride, magnesium chloride, and calcium chloride), and chloride salts plus corrosion inhibitors (i.e., sodium nitrite and di-Sodium hydrogen phosphate) during the time of preparation. Cylindrical reinforced concrete specimens with a centrally embedded steel bar were prepared from different concrete mixes. Corrosion tests, i.e., half-cell potential (HCP) and linear polarization resistance (LPR) measurements were performed on the cylindrical specimens at regular intervals up to 854 days. Chloride analysis and microstructure analysis were carried out on the concrete powder samples collected from near the rebar level of cylindrical specimens at the age of 854 days. From the obtained results, the variations in free chloride ion (C_F) content and bound chloride ion (C_B) content in concrete with cation type of chloride ions and corrosion inhibitors are analyzed. Further, the effects of cation type of chloride ions and corrosion inhibitors on variations in corrosion parameters of steel reinforcement in concrete in the presence of internal chloride are evaluated. In addition, the changes in microstructure of concrete in the presence of internal chloride and corrosion inhibitors are analyzed through the obtained results from X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and Field emission scanning electron microscope (FESEM) analyses.

5.2 Chloride content

The obtained free chloride ion and bound chloride ion contents of concrete powder samples collected from near the rebar level i.e., at depth interval of 25-30 mm of cylindrical specimens containing chloride salts and corrosion inhibitors, at the age of 854 days are presented in Table 5.1. It is to be noted that the bound chloride content was calculated as the difference of total chloride and free chloride contents.

Table 5.1 Free and bound chloride ion contents of different concrete mixes

Cement	Admixed chloride salt and corrosion inhibitor content (% by weight of cement)	Chloride content (% by weight of concrete)		Cement	Admixed chloride salt and corrosion inhibitor content (% by weight of cement)	Chloride content (% by weight of concrete)	
		Free chloride ion (C_F) content	Bound chloride ion (C_B) content			Free chloride ion (C_F) content	Bound chloride ion (C_B) content
OPC	3.5NC	0.315	0.073	PPC	3.5NC	0.337	0.031
	3.5MC	0.140	0.091		3.5MC	0.156	0.080
	3.5CC	0.202	0.102		3.5CC	0.248	0.079
	3.5NC+3SN	0.301	0.085		3.5NC+3SN	0.322	0.054
	3.5MC+3SN	0.137	0.104		3.5MC+3SN	0.146	0.084
	3.5CC+3SN	0.196	0.121		3.5CC+3SN	0.201	0.107
	3.5NC+3DHP	0.251	0.114		3.5NC+3DHP	0.306	0.061
	3.5MC+3DHP	0.113	0.103		3.5MC+3DHP	0.123	0.095
	3.5CC+3DHP	0.173	0.141		3.5CC+3DHP	0.183	0.111

NC: sodium chloride; MC: magnesium chloride; CC: calcium chloride; SN: sodium nitrite;

DHP: di-Sodium hydrogen phosphate

From Table 5.1, it is observed that the free chloride ion (C_F) content near rebar level is slightly lower in the concrete containing both chloride salt and corrosion inhibitor as compared to that containing only chloride salt irrespective of cement type and cation type of admixed chloride salt. This may be attributed to the fact that the addition of corrosion inhibitors increased the binding of chloride ions thereby leading to higher bound chloride ion (C_B) content in the concrete containing both chloride salt and corrosion inhibitor than that containing only chloride salt for both cements as evident from Table 5.1. The higher chloride binding in the presence of corrosion inhibitors may be due to the effect of reaction of chloride ions with hydrated cement phases to a comparatively higher extent. The higher chloride binding in the presence of corrosion inhibitors is further corroborated with the results of XRD and FESEM analysis (Fig. 5.7 to Fig. 5.14, discussed later), which indicated presence of more amount of Friedel's salt (calcium chloroaluminate) in the concrete admixed with both chloride salt and corrosion inhibitor as compared to that admixed with only chloride salt. While comparing the effect of corrosion inhibitor on free and bound chloride contents, it is observed that the sodium nitrite added concrete mixes showed higher free chloride content and lower bound chloride content than that added with di-Sodium

hydrogen phosphate (DHP). The dominant effect of higher extent of chloride binding in the presence of phosphate ions resulted in less free chloride content in the concrete admixed with DHP as compared to that admixed with sodium nitrite (NaNO_2). As reported in the literature, presence of phosphate ions in concrete increases the formation of Friedel's salt thereby increasing the amount of bound chloride [105]. In the present study, the formation of higher amount of Friedel's salt in the concrete added with DHP than that added with NaNO_2 was evident from the results of XRD analysis shown in Fig. 5.7 and Fig. 5.8, where the weight (%) of Friedel's salt were higher in DHP added concrete than sodium nitrite added concrete. In addition, the formation of chlorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{Cl}$) in the combined presence of phosphate and chloride ions further increases the binding of chloride ions in DHP added concrete as compared to sodium nitrite added concrete.

From the results of free chloride ion (C_F) content shown in Table 5.1, for both OPC and PPC, the NaCl added concrete mixes showed 1.52 times, and 2.23 times higher free chloride content than that added with CaCl_2 , and MgCl_2 respectively irrespective of the addition of corrosion inhibitors. The significantly higher free chloride content of concrete added with NaCl than CaCl_2 may be attributed to the effect of release of higher amount of $(\text{OH})^-$ ions in the pore solution of concrete added with NaCl as compared to CaCl_2 during the formation of Friedel's salt through anion-exchange mechanism [30, 180]. The release of higher amount of $(\text{OH})^-$ ions in the pore solution of concrete added with NaCl may compete with Cl^- ions to a greater degree thereby resulting in lower adsorption of Cl^- ions in the interlayers of the principle layer of AFm structure in the process of Friedel's salt formation through adsorption mechanism [180]. In case of concrete added with CaCl_2 , the release of lower amount of $(\text{OH})^-$ ions in the pore solution during the formation of Friedel's salt through anion-exchange mechanism may compete with Cl^- ions to a lower extent thereby resulting in higher adsorption of Cl^- ions in the interlayers of the principal layer of AFm structure [180]. This leads to formation of more amount of Friedel's salt thereby higher chloride binding, and lower free chloride content in the concrete containing CaCl_2 than NaCl. The higher chloride binding in the concrete admixed with CaCl_2 as compared to that admixed with NaCl is evident from the bound chloride content values shown in Table 5.1. The presence of more amount of Friedel's salt in the concrete containing CaCl_2 than NaCl was evident from the results of XRD analysis shown in Fig. 5.7 and Fig. 5.8, where the weight (%) of Friedel's salt were higher in CaCl_2 added concrete than that in NaCl added concrete. In addition, the FESEM images shown in Fig. 5.9 and Fig. 5.11 for

OPC, and Fig. 5.12 and Fig. 5.14 for PPC further corroborates the results obtained from chloride analysis and XRD patterns where more amount of Friedel's salt formation (through small hexagonal crystals) was observed in the concrete containing CaCl_2 than NaCl . Further, there may be higher extent of physical binding of chloride ions with calcium silicate hydrate (C-S-H) in the concrete containing CaCl_2 as compared to that containing NaCl [181]. Between MgCl_2 and CaCl_2 , the free chloride content was lower in the concrete containing MgCl_2 as compared to that containing CaCl_2 irrespective of cement type and presence of corrosion inhibitors. Further, the bound chloride content was also lower in case of MgCl_2 than CaCl_2 , which may be due to lower total chloride content in the concrete added with MgCl_2 than that added with CaCl_2 . The lower free chloride content in the concrete containing MgCl_2 than CaCl_2 may be due to the dominant effect of formation of magnesium oxychloride as well as formation of higher amount of calcium hypochlorite in the presence of MgCl_2 thereby reducing the amount of free chloride in the concrete containing MgCl_2 [30]. The presence of more amount of calcium hypochlorite in the concrete containing MgCl_2 than CaCl_2 is evident from the XRD patterns shown in Fig. 5.1 to Fig. 5.6, where the peak intensity of calcium hypochlorite (observed at $39.4^\circ 2\theta$) was higher in the concrete added with MgCl_2 than CaCl_2 . The higher bound chloride content in case of CaCl_2 than MgCl_2 may be attributed to the dominant effect of higher extent of physical binding of chloride ions with calcium silicate hydrate (C-S-H) in the concrete added with CaCl_2 as compared to that added with MgCl_2 . In case of concrete added with MgCl_2 , the conversion of C-S-H into non-cementitious M-S-H (magnesium silicate hydrate) in the presence Mg^{2+} ions results in lower extent of physical binding of chloride ions with C-S-H. Further, there was formation of more amount of Friedel's salt in the concrete containing CaCl_2 , which is substantiated by higher weight (%) of Friedel's salt in the concrete containing CaCl_2 than MgCl_2 as observed from the results of XRD analysis (Fig. 5.7 and Fig. 5.8). The results of chloride content presented in Table 5.1 indicated that the free chloride content was more in PPC concrete mixes than OPC concrete mixes whereas the opposite variation was observed in chloride binding i.e., bound chloride content was higher in OPC concrete as compared to PPC concrete irrespective of admixed chloride salts, and corrosion inhibitors. The higher bound chloride content in OPC concrete than PPC concrete may be attributed to the significant effect of binding of chloride ions with hydrated C_3A to a greater extent as a result of more C_3A content in OPC thereby lowering free chloride content in OPC concrete [181]. More bound chloride content in the concrete mixes prepared from OPC than PPC is further corroborated with the results of

XRD analysis (Fig. 5.7 and Fig. 5.8), where the weight (%) of Friedel's salt were higher in the concrete made from OPC than that made from PPC. Similarly, the FESEM images (Fig. 5.9 to Fig. 5.14) showed more formation of Friedel's salt, appeared as small hexagonal crystals, in OPC concrete than that in PPC concrete.

5.3 Microstructure of concrete

As stated earlier, the microstructure of concrete admixed with only chloride salt and that admixed with both chloride salt and corrosion inhibitor was studied through XRD, FESEM, and FTIR analyses. The XRD patterns, and weight (%) of different compounds formed in the concrete mixes are shown in Fig. 5.1 to Fig. 5.8. Similarly, the FESEM images and FTIR spectra obtained from different concrete mixes are presented in Fig. 5.9 to Fig. 5.14, and Fig. 5.15 to Fig. 5.20 respectively.

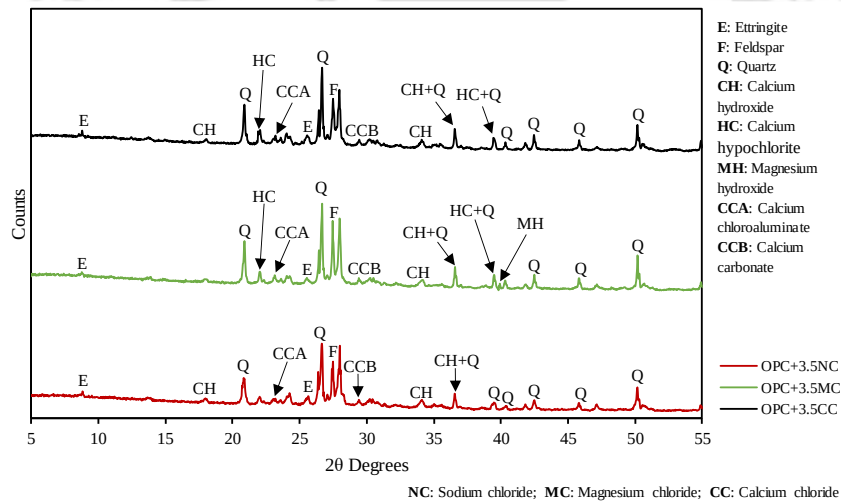


Fig. 5.1 XRD patterns of concrete prepared with OPC and admixed with different chloride salts

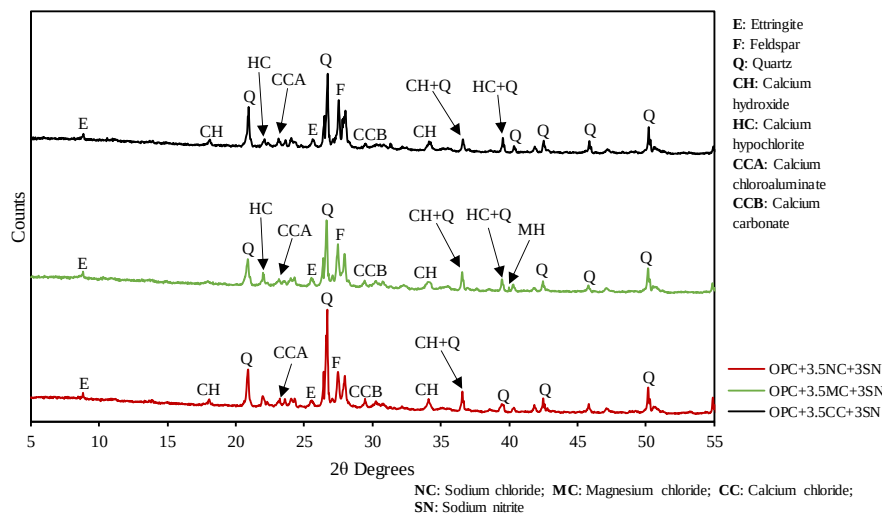


Fig. 5.2 XRD patterns of concrete prepared with OPC and admixed with different chloride salts and sodium nitrite

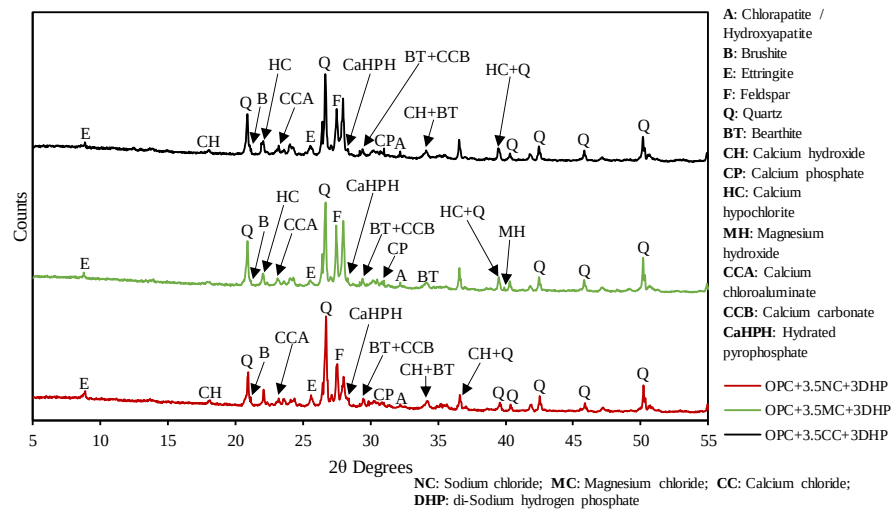


Fig. 5.3 XRD patterns of concrete prepared with OPC and admixed with different chloride salts and di-Sodium hydrogen phosphate

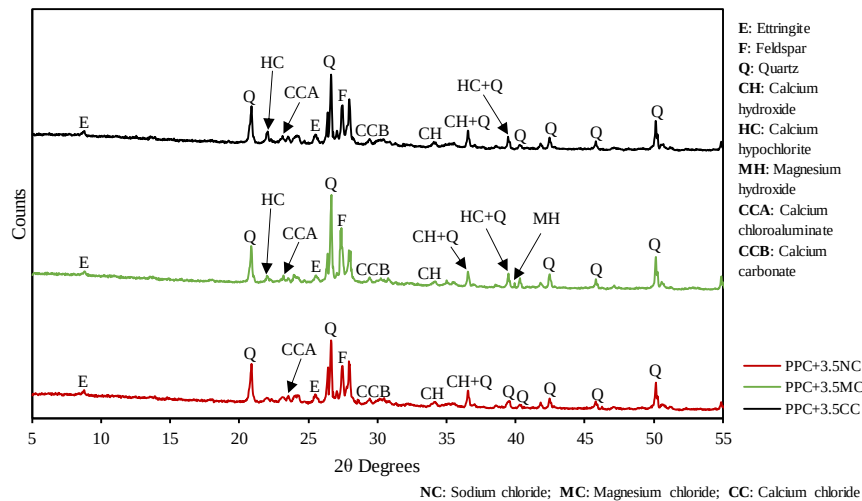


Fig. 5.4 XRD patterns of concrete prepared with PPC and admixed with different chloride salts

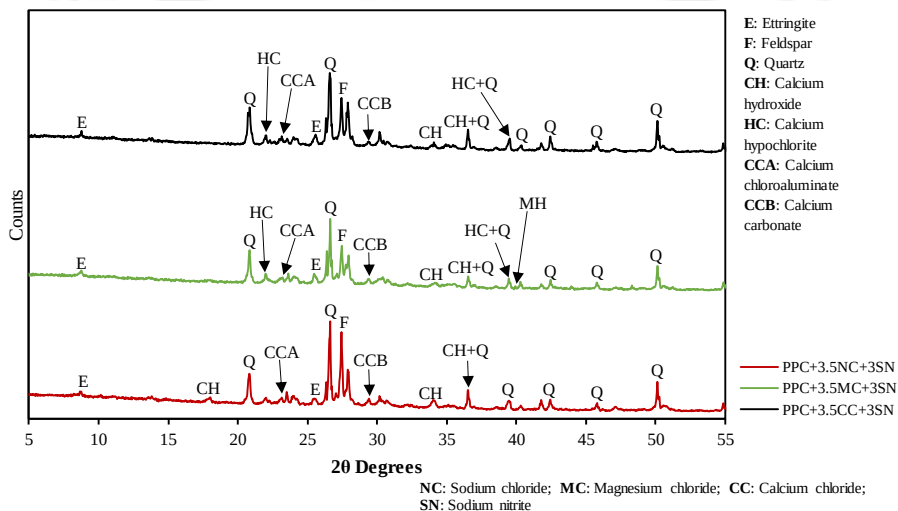


Fig. 5.5 XRD patterns of concrete prepared with PPC and admixed with different chloride salts and sodium nitrite

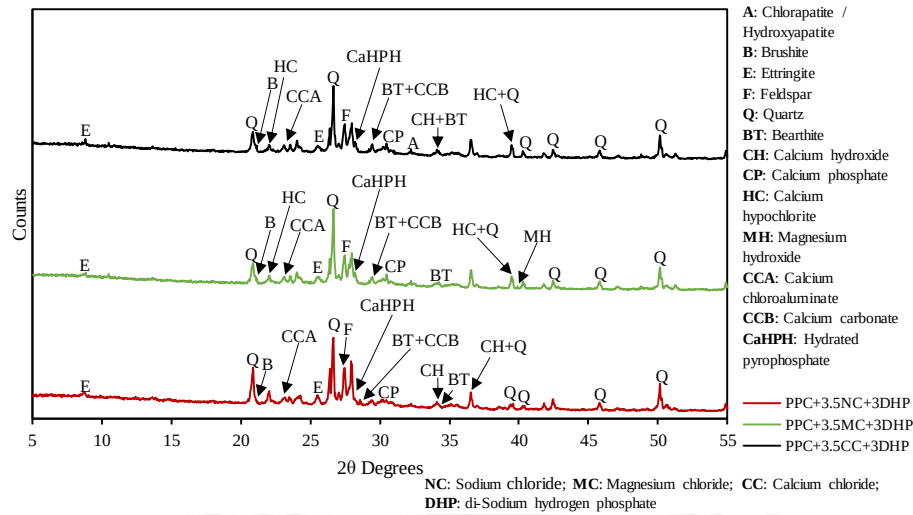


Fig. 5.6 XRD patterns of concrete prepared with PPC and admixed with different chloride salts and di-Sodium hydrogen phosphate

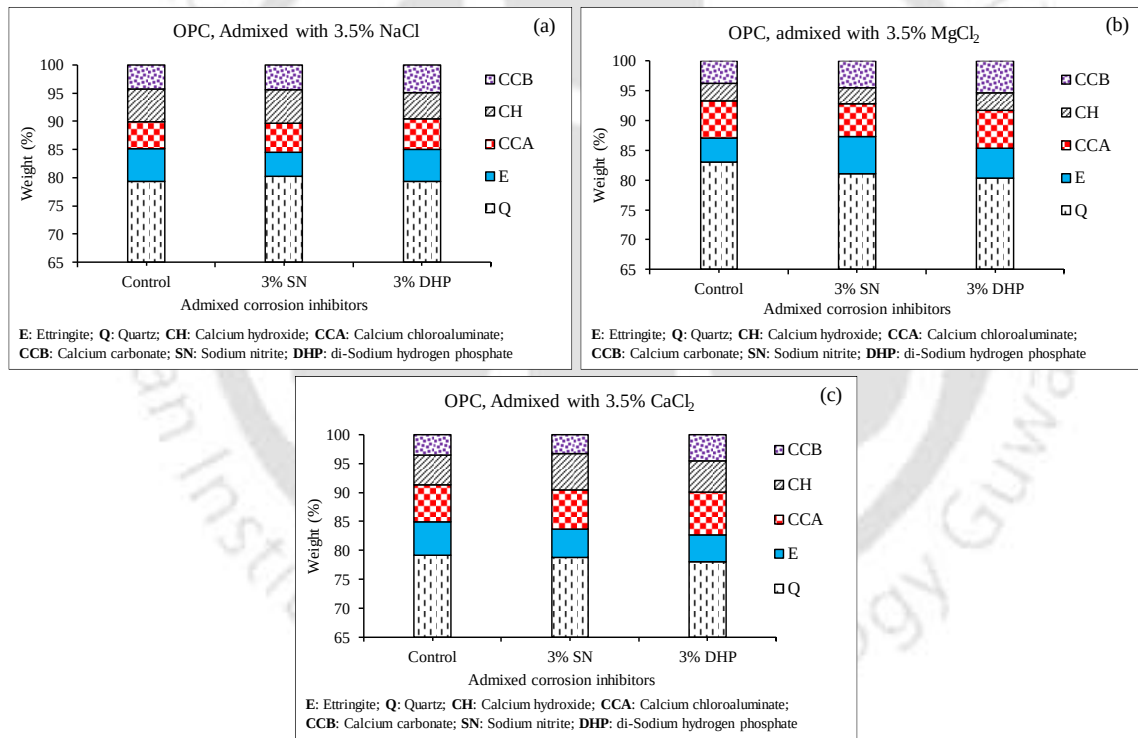


Fig. 5.7 Weight (%) of compounds obtained from XRD patterns of OPC control concrete and concrete admixed with corrosion inhibitors: (a) 3.5% NaCl, (b) 3.5% MgCl₂, and (c) 3.5% CaCl₂

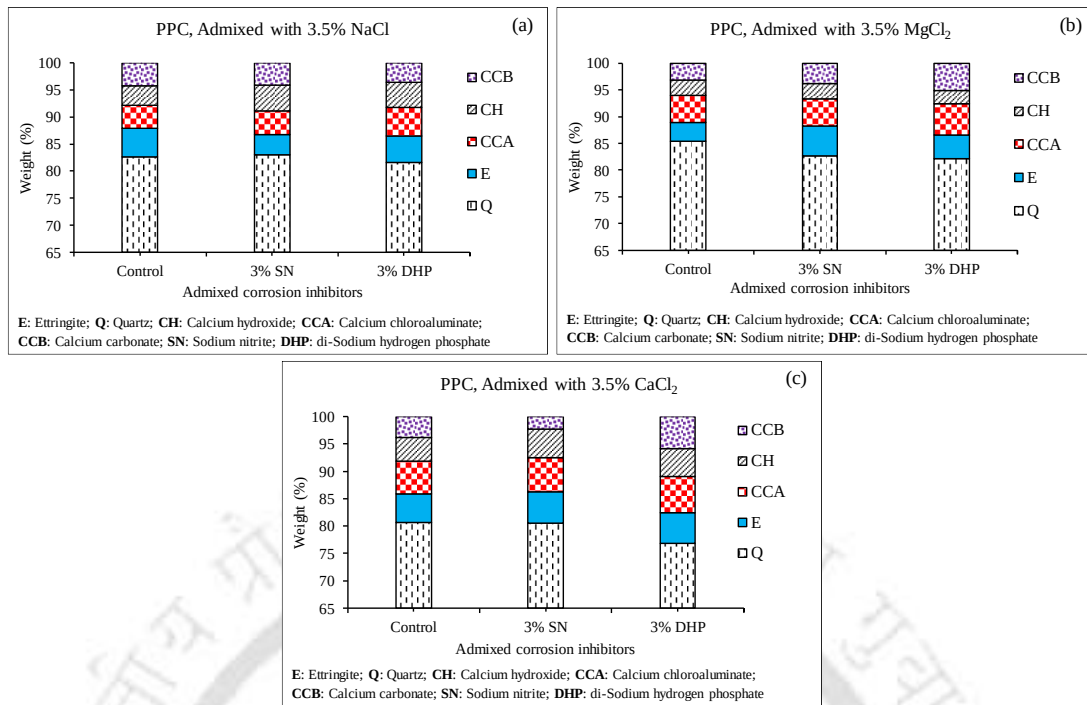


Fig. 5.8 Weight (%) of compounds obtained from XRD patterns of PPC control concrete and concrete admixed with corrosion inhibitors: (a) 3.5% NaCl, (b) 3.5% MgCl₂, and (c) 3.5% CaCl₂

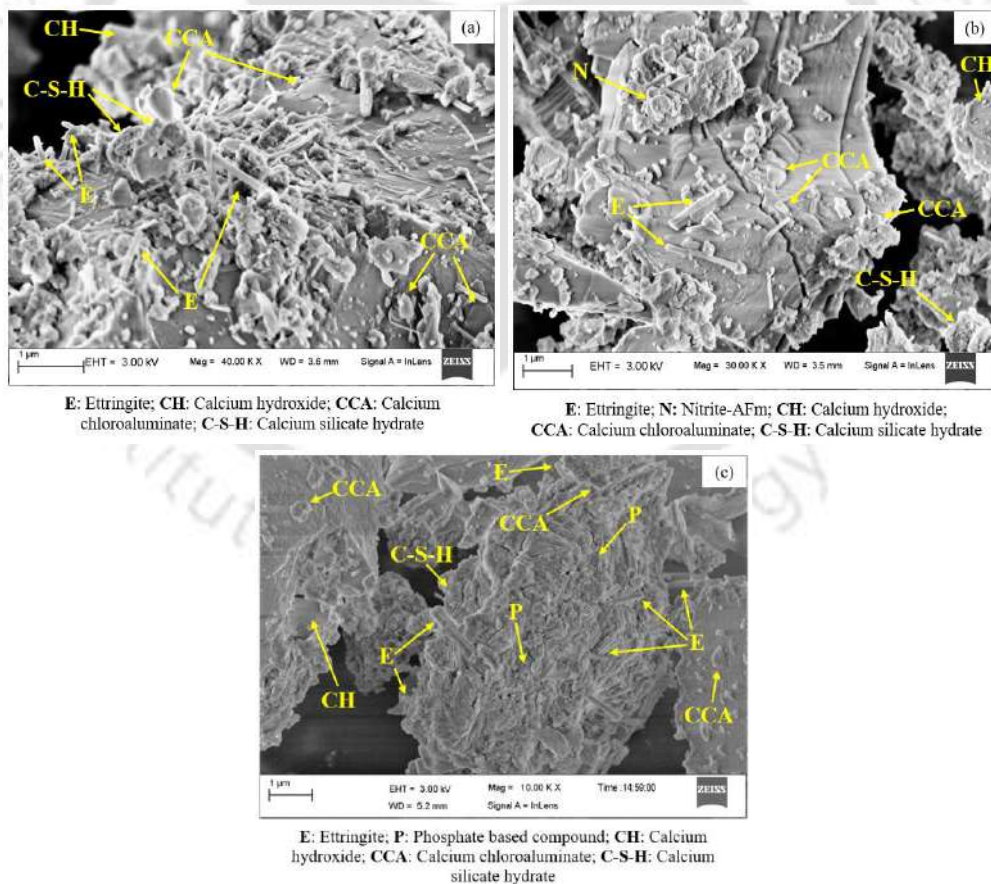


Fig. 5.9 FESEM images of concrete prepared from OPC: (a) concrete admixed with 3.5% NaCl, (b) concrete admixed with 3.5% NaCl and 3% NaNO₂, and (c) concrete admixed with 3.5% NaCl and 3% DHP

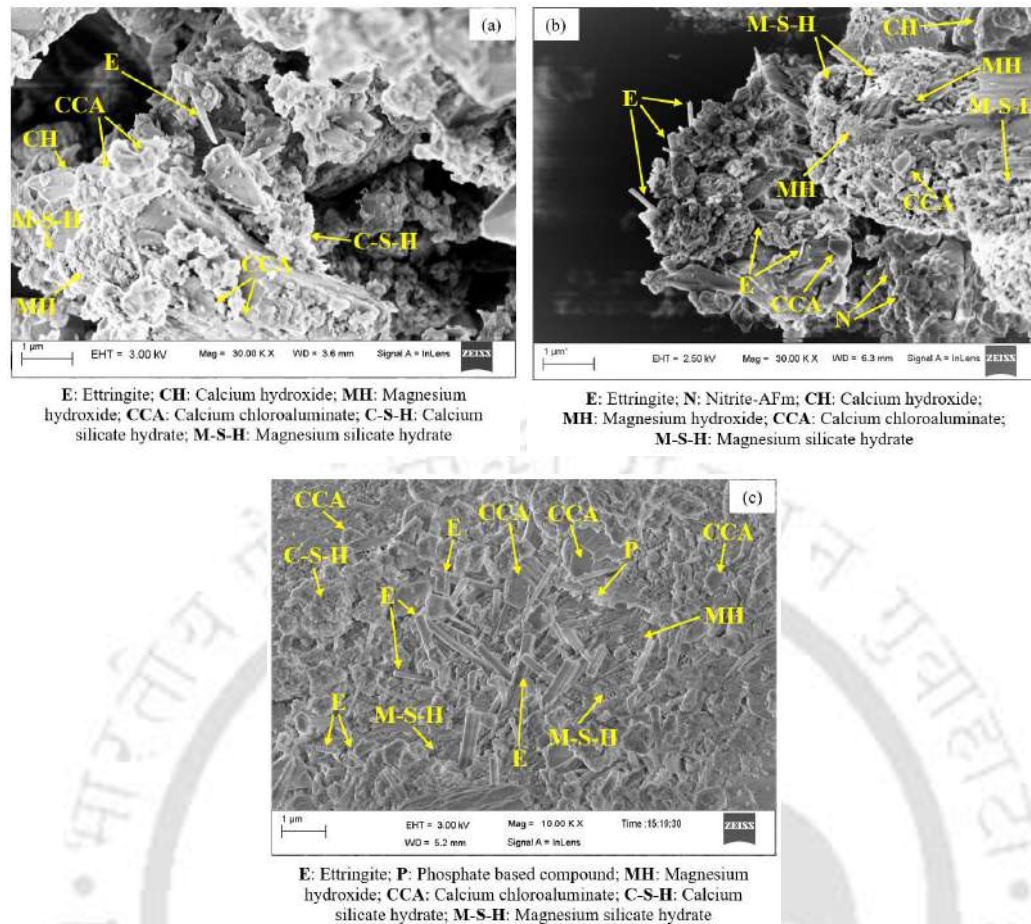
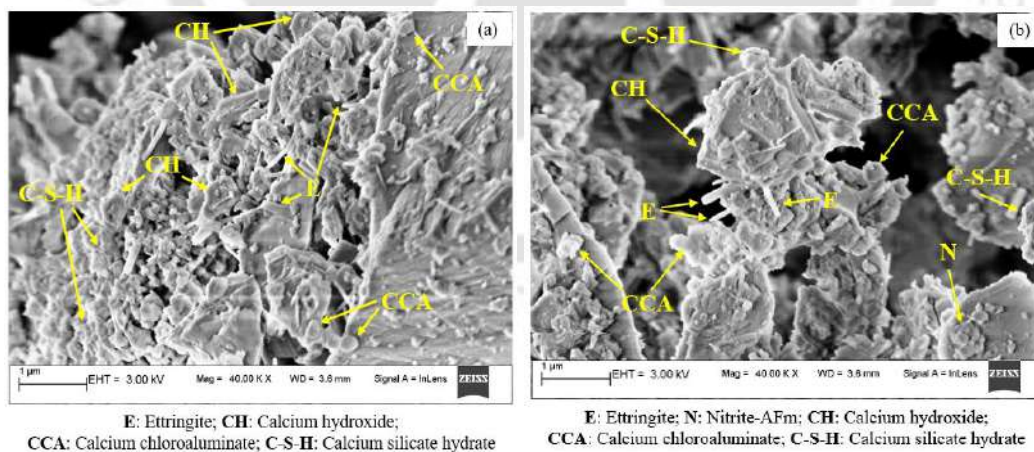


Fig. 5.10 FESEM images of concrete prepared from OPC: (a) concrete admixed with 3.5% MgCl_2 , (b) concrete admixed with 3.5% MgCl_2 and 3% NaNO_2 , and (c) concrete admixed with 3.5% MgCl_2 and 3% DHP



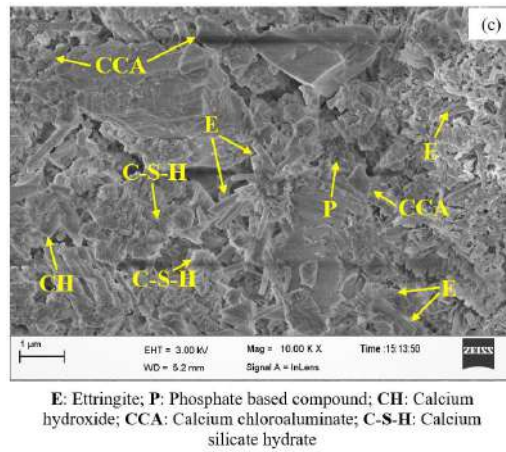


Fig. 5.11 FESEM images of concrete prepared from OPC: (a) concrete admixed with 3.5% CaCl_2 , (b) concrete admixed with 3.5% CaCl_2 and 3% NaNO_2 , and (c) concrete admixed with 3.5% CaCl_2 and 3% DHP

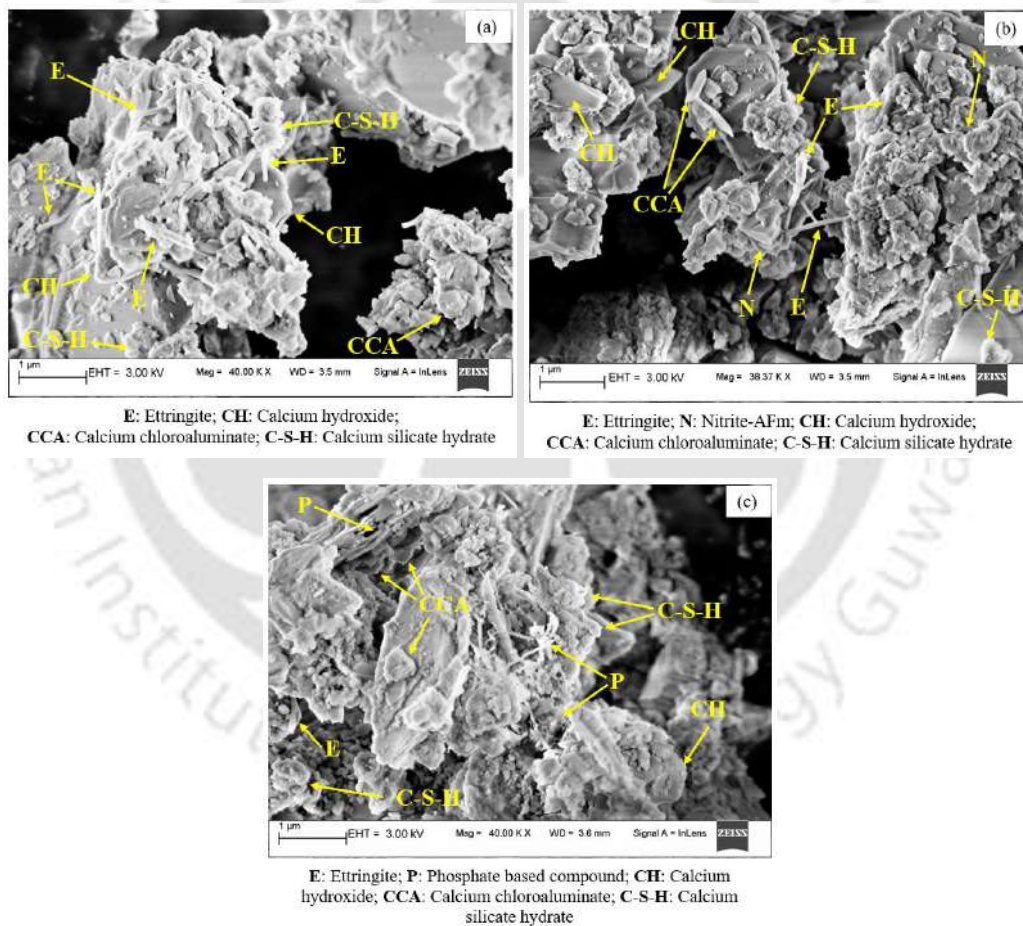


Fig. 5.12 FESEM images of concrete prepared from PPC: (a) concrete admixed with 3.5% NaCl , (b) concrete admixed with 3.5% NaCl and 3% NaNO_2 , and (c) concrete admixed with 3.5% NaCl and 3% DHP

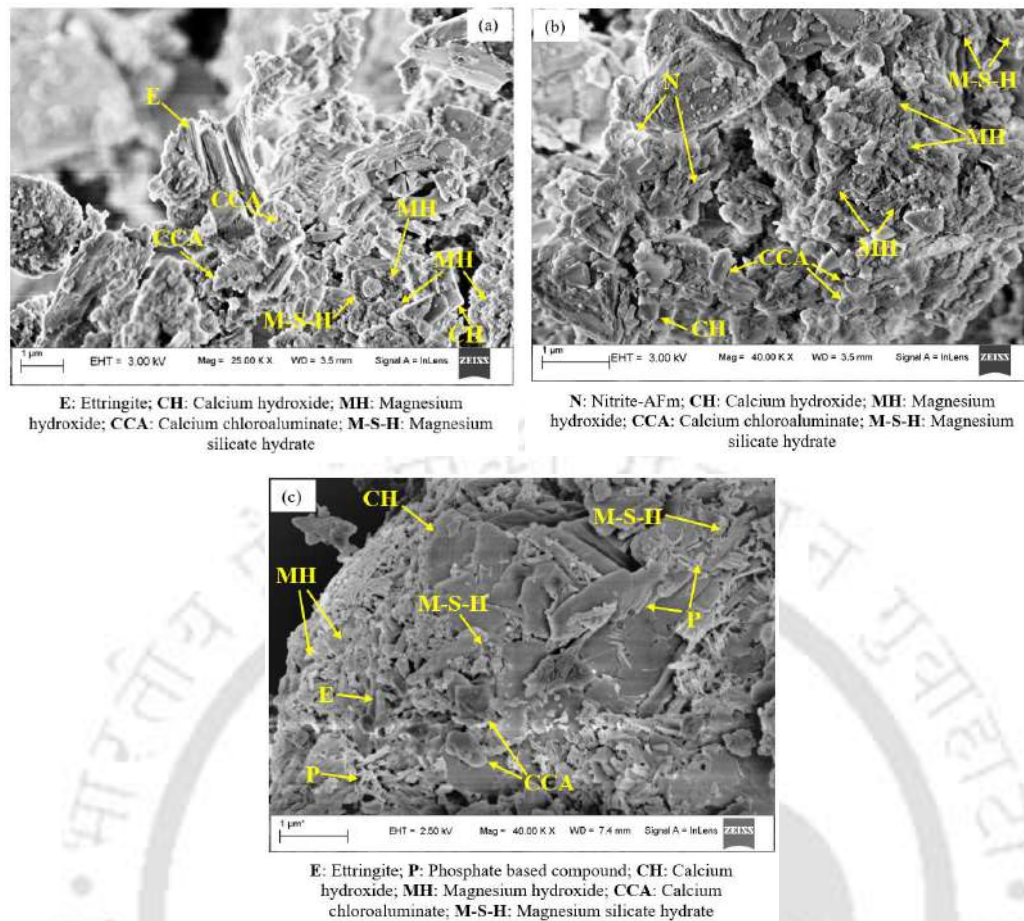
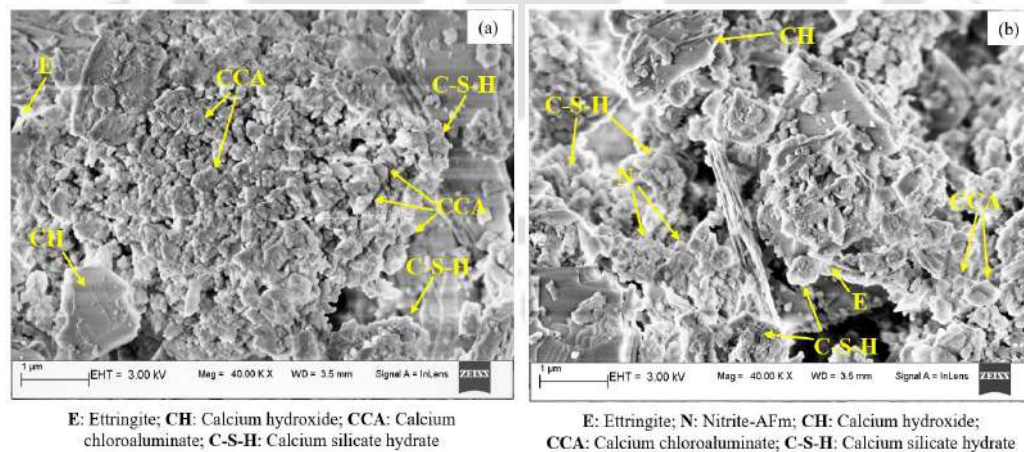


Fig. 5.13 FESEM images of concrete prepared from PPC: (a) concrete admixed with 3.5% MgCl_2 , (b) concrete admixed with 3.5% MgCl_2 and 3% NaNO_2 , and (c) concrete admixed with 3.5% MgCl_2 and 3% DHP



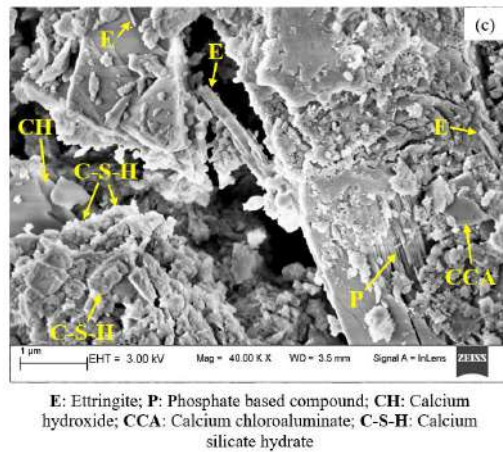


Fig. 5.14 FESEM images of concrete prepared from PPC: (a) concrete admixed with 3.5% CaCl_2 , (b) concrete admixed with 3.5% CaCl_2 and 3% NaNO_2 , and (c) concrete admixed with 3.5% CaCl_2 and 3% DHP

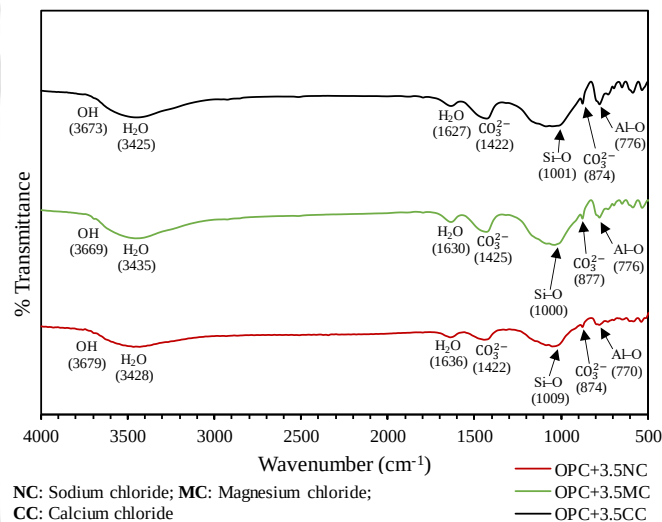


Fig. 5.15 FTIR spectra of concrete prepared with OPC and admixed with different chloride salts

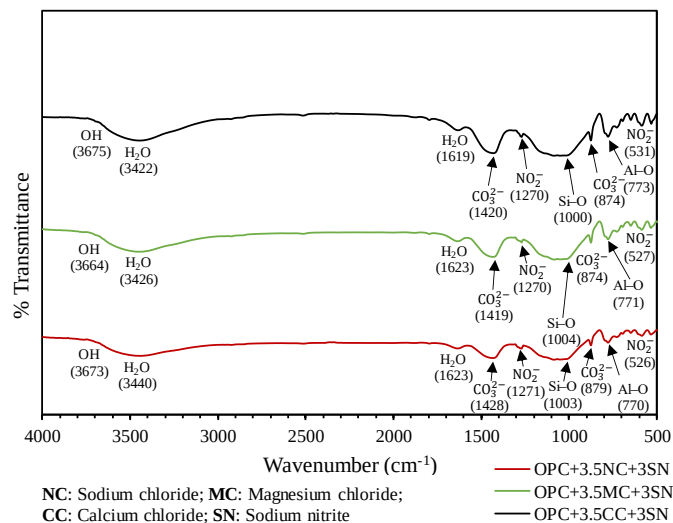


Fig. 5.16 FTIR spectra of concrete prepared with OPC and admixed with different chloride salts and sodium nitrite

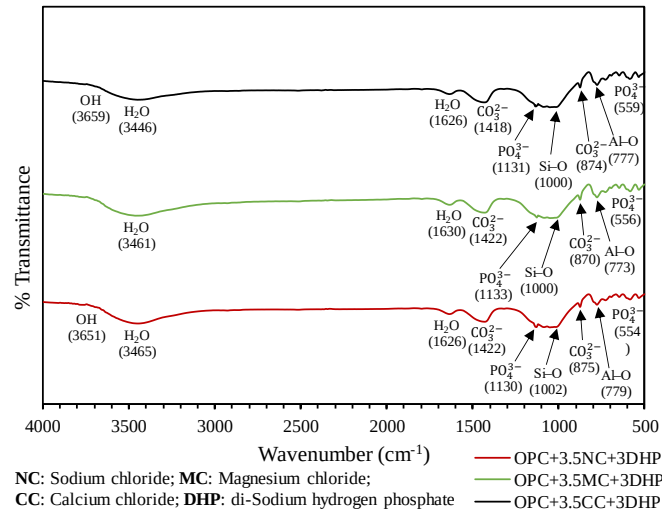


Fig. 5.17 FTIR spectra of concrete prepared with OPC and admixed with different chloride salts and di-Sodium hydrogen phosphate

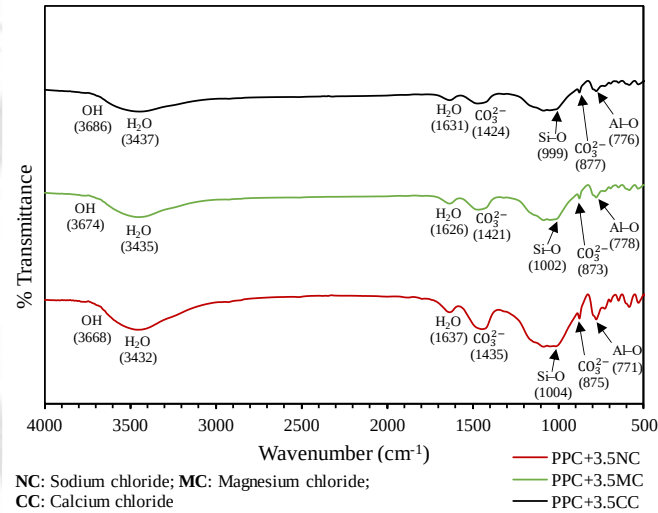


Fig. 5.18 FTIR spectra of concrete prepared with PPC and admixed with different chloride salts

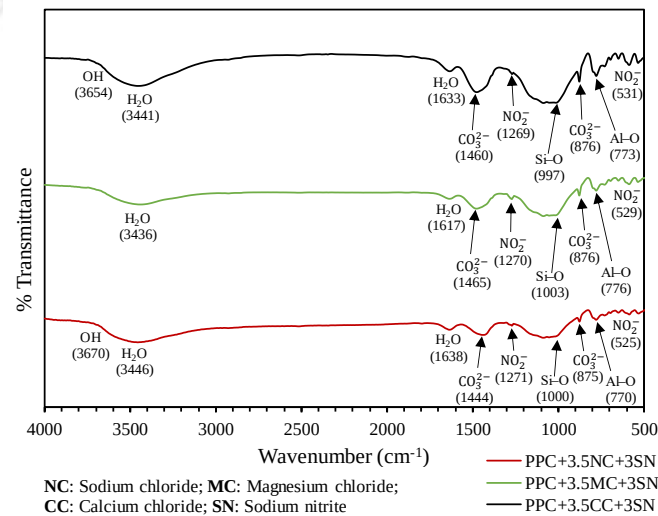


Fig. 5.19 FTIR spectra of concrete prepared with PPC and admixed with different chloride salts and sodium nitrite

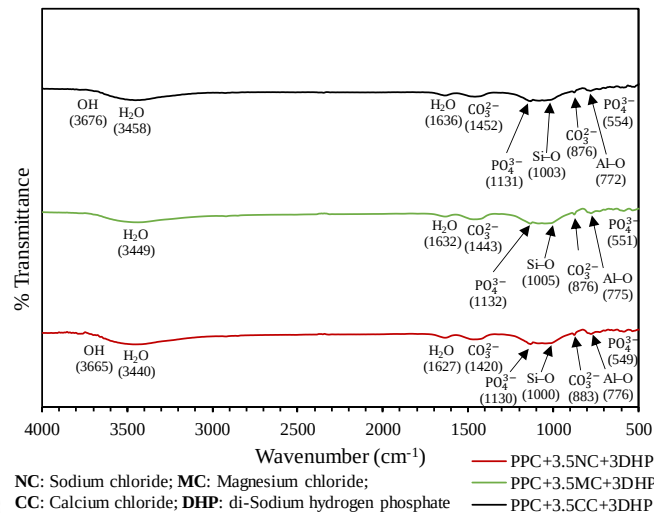


Fig. 5.20 FTIR spectra of concrete prepared with PPC and admixed with different chloride salts and di-Sodium hydrogen phosphate

5.3.1 Effect of corrosion inhibitor on microstructure of concrete

In the XRD patterns (in Fig. 5.1 to Fig. 5.6), peaks corresponding to calcium hydroxide (CH) were found at $18.02^\circ 2\theta$, $34.1^\circ 2\theta$, and $36.5^\circ 2\theta$ in both OPC and PPC concrete mixes irrespective of added chloride salt and corrosion inhibitor. The presence of calcium hydroxide in all the concrete mixes was further substantiated through FESEM images illustrated in Fig. 5.9 to Fig. 5.14, where calcium hydroxide appeared as large hexagonal shape crystals. Similarly, in the FTIR spectra illustrated in Fig. 5.15 to Fig. 5.20, the stretching vibration of O–H band observed between $3654 - 3686 \text{ cm}^{-1}$ indicated the presence of calcium hydroxide in both OPC and PPC concrete. The concrete mixes admixed with both chloride salt and corrosion inhibitor mostly showed higher weight (%) of calcium hydroxide as compared to those admixed with only chloride salt. This may be ascribed to the effect of precipitation of calcium hydroxide to a comparatively higher extent in the presence of corrosion inhibitors in concrete. Between the corrosion inhibitors, the presence of calcium hydroxide (CH) was mostly higher in the concrete added with NaNO_2 as compared to that added with DHP as evident from the weight (%) of calcium hydroxide obtained from the results of XRD analysis shown in Fig. 5.7 and Fig. 5.8. In the presence of DHP, phosphate based compounds are formed, which consume calcium hydroxide thereby reducing its amount in the concrete mixes added with DHP as compared to NaNO_2 . The main phases of phosphate based compounds identified in the XRD patterns were calcium phosphate at $27.76^\circ 2\theta$ and $31.02^\circ 2\theta$; bearthite at $29.2^\circ 2\theta$ and $34.9^\circ 2\theta$; chlorapatite/ hydroxyapatite at $32.29^\circ 2\theta$; hydrated pyrophosphate at $28.4^\circ 2\theta$; and brushite

at $20.94^\circ 2\theta$. The presence of phosphate based compounds in the concrete added with DHP was further substantiated through the FESEM images shown in Fig. 5.9 (c), Fig. 5.10 (c), Fig. 5.11 (c), Fig. 5.12 (c), Fig. 5.13 (c), and Fig. 5.14 (c), and FTIR spectra illustrated in Fig. 5.17 and Fig. 5.20. In the FESEM images, the morphology of phosphate based compounds appeared in the form of rod-shaped structures. In the FTIR spectra, the presence of phosphate based compounds was confirmed through P=O stretching bands appeared between $1130 - 1133 \text{ cm}^{-1}$, and out of plane bending of P–OH appeared in the range $549 - 559 \text{ cm}^{-1}$ for both OPC and PPC mixes.

The presence of calcium chloroaluminate (CCA) in the concrete mixes was confirmed through the peaks observed at $11.2^\circ 2\theta$ and $23.2^\circ 2\theta$ in the XRD patterns shown in Fig. 5.1 to Fig. 5.6 irrespective of cement type, chloride salts and corrosion inhibitors. In addition, the FESEM images shown in Fig. 5.9 to Fig. 5.14 further substantiate the formation of calcium chloroaluminate in the concrete mixes appeared as small hexagonal crystals. The results of XRD analysis showed that the addition of corrosion inhibitors enhanced the formation of calcium chloroaluminate (CCA) as the weight (%) of CCA was mostly higher in the concrete mixes added with chloride salt plus corrosion inhibitor than that added with only chloride salt. In comparison to NaNO_2 added mixes, the DHP added mixes mostly showed higher weight (%) of calcium chloroaluminate thereby indicating its more formation in DHP than NaNO_2 admixed concrete mixes. This indicates that the presence of DHP favours the formation of calcium chloroaluminate to a comparatively higher extent. The formation of nitrite based compound in the concrete added with NaNO_2 was confirmed through FESEM images shown in Fig. 5.9 (b), Fig. 5.10 (b), Fig. 5.11 (b), Fig. 5.12 (b), Fig. 5.13 (b), and Fig. 5.14 (b); and FTIR spectra shown in Fig. 5.16 and Fig. 5.19. In FESEM images, the nitrite based compound appeared in the form of petal shaped crystals, and in FTIR spectra, the asymmetric stretching vibration of nitrite appeared in the range of $1269 - 1271 \text{ cm}^{-1}$, and bending vibration of nitrite appeared in the range of $525 - 531 \text{ cm}^{-1}$.

5.3.2 Effect of cation type of chloride salt on microstructure of concrete

Among the chloride salts, the formation of calcium hydroxide (CH) and calcium chloroaluminate (CCA) were mostly higher in the concrete mixes added with CaCl_2 as compared to other chloride salts as evident from the weight (%) of calcium hydroxide, and calcium chloroaluminate obtained from the results of XRD analysis. These observations are in line with the results obtained from FESEM analysis where more formation of calcium hydroxide and calcium chloroaluminate were observed in the concrete added with CaCl_2

than that added with NaCl, and MgCl₂. In concrete, the presence of CaCl₂ results in additional formation of calcium hydroxide [56], and reduces its leaching velocity [37]. This may be the reason behind higher Ca(OH)₂ content in the concrete added with CaCl₂ as compared to NaCl, and MgCl₂. More amount of calcium chloroaluminate (CCA) in the concrete added with CaCl₂ than MgCl₂ and NaCl may be attributed to the fact that the reaction of chloride ions with C₃A might have occurred to a comparatively greater extent in the presence of Ca²⁺ ions than Mg²⁺ and Na⁺ ions. Further, between NaCl, and MgCl₂, the formation of calcium hydroxide (CH) was lower in MgCl₂ added concrete mixes, whereas the formation of calcium chloroaluminate (CCA) was lower in NaCl added concrete mixes, irrespective of cement type and corrosion inhibitors. The lower calcium hydroxide content in the concrete containing MgCl₂ may be attributed to the formation of magnesium hydroxide and calcium hypochlorite in the presence of MgCl₂ that consume a large portion of Ca(OH)₂. In the XRD patterns (Fig. 5.1 to Fig. 5.6), magnesium hydroxide (MH) was identified at 39.92° 2θ, and calcium hypochlorite was identified at 21.7° 2θ, and 39.4° 2θ in the concrete mixes added with MgCl₂. The FESEM images shown in Fig. 5.10 and Fig. 5.13 also indicated the formation of magnesium hydroxide in the concrete mixes added with MgCl₂ in the form of rosette-like clusters. Further, lower calcium chloroaluminate content in the concrete mixes added with NaCl as compared to MgCl₂ and CaCl₂ may be attributed to the effect of release of higher concentration of (OH)⁻ ions in the pore solution of concrete added with NaCl that compete with chloride ions thereby reducing the formation of calcium chloroaluminate.

5.3.3 Effect of cement type on microstructure of concrete

From the results of XRD analysis (Fig. 5.7 and Fig. 5.8), it is observed that the weight (%) of calcium hydroxide (CH) and calcium chloroaluminate (CCA) were mostly higher in OPC concrete as compared to PPC concrete irrespective of type of chloride salt and corrosion inhibitor. The formation of higher amount of calcium hydroxide and calcium chloroaluminate in OPC concrete than PPC concrete was also evident from the FESEM images shown in Fig. 5.9 to Fig. 5.14. In PPC concrete, the consumption of calcium hydroxide in pozzolanic reaction results in its availability in lower amount than OPC concrete. The higher calcium chloroaluminate content in OPC concrete as compared to PPC concrete may be due to the effect of reaction of chloride ions with C₃A to a comparatively higher extent as a result of more C₃A content in OPC than PPC.

In the XRD patterns shown in Fig. 5.1 to Fig. 5.6, the peaks of different phases such as ettringite (E) at $8.8^\circ 2\theta$ and $25.6^\circ 2\theta$; quartz (Q) at $20.8^\circ 2\theta$, $26.64^\circ 2\theta$, $39.45^\circ 2\theta$, $42.45^\circ 2\theta$, $45.5^\circ 2\theta$ and $50.2^\circ 2\theta$; feldspar (F) at $27.5^\circ 2\theta$; and calcium carbonate (CCB) at $29.4^\circ 2\theta$ were observed in both OPC and PPC concrete mixes irrespective of admixed chloride salt and corrosion inhibitor. Similarly, calcium silicate hydrate (C-S-H) in the form of cotton-shaped structure, and ettringite in the shape of needle shaped crystals were observed in the FESEM images shown in Fig. 5.9 to Fig. 5.14. In the FTIR spectra shown in Fig. 5.15 to Fig. 5.20, the presence of ettringite (E) was substantiated by Al-O peaks observed between $770 - 779 \text{ cm}^{-1}$ in OPC concrete and that between $770 - 778 \text{ cm}^{-1}$ in PPC concrete. Further, strong bands appearing at around $1418 - 1465 \text{ cm}^{-1}$ in both OPC and PPC concrete are associated with ν_3 vibration of CO_3^{2-} , which confirms the presence of calcium carbonate (CaCO_3) in the concrete mixes. In addition, ν_2 vibration of CO_3^{2-} appeared in the range of $870 - 883 \text{ cm}^{-1}$ in both OPC and PPC concrete mixes. The FESEM images indicated more formation of C-S-H in PPC concrete as compared to OPC concrete irrespective of the presence of chloride salts and corrosion inhibitors as evident from Fig. 5.9 to Fig. 5.14. This may be attributed to the effect of pozzolanic reaction that results in more formation of C-S-H in PPC concrete as compared to OPC concrete. The presence of C-S-H in the concrete mixes was further confirmed through the asymmetric stretching vibration of Si-O observed between $997 - 1009 \text{ cm}^{-1}$ in the FTIR spectra (Fig. 5.15 to Fig. 5.20).

5.4 Corrosion parameters

The obtained half-cell potential (E_0) and corrosion current density (I_{corr}) of steel reinforcement in cylindrical reinforced concrete specimens made from OPC and PPC, and admixed with chloride salts, and chloride salts plus corrosion inhibitors are shown in Fig. 5.21 to Fig. 5.24. Each value of half-cell potential and corrosion current density shown in these figures are the average value of three replicate cylindrical specimens. From Fig. 5.21 and Fig. 5.22, it is observed that the obtained half-cell potential values of embedded steel reinforcement in concrete were mostly less negative than -270 mV/SCE at all ages irrespective of cement type, admixed chloride salt, and presence of corrosion inhibitors thereby indicating lower probability of occurrence of steel reinforcement corrosion as per ASTM C876-15 [182].

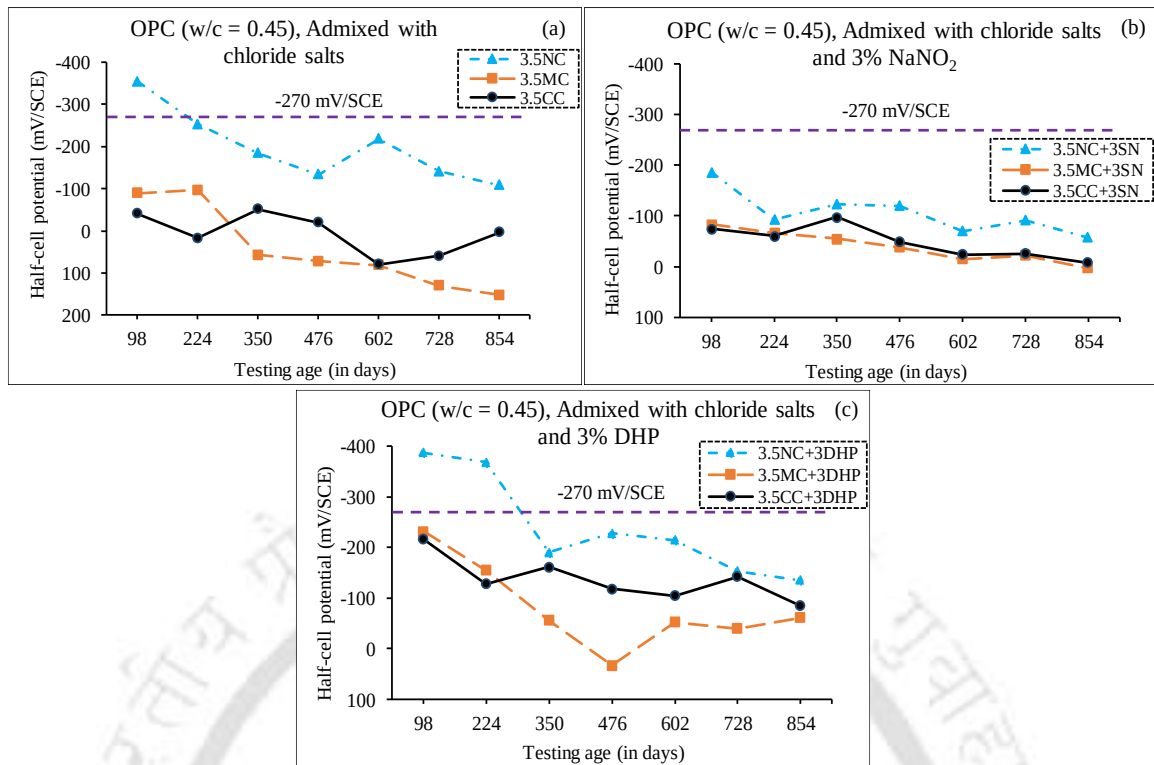


Fig. 5.21 Half-cell potential of reinforcing steel in OPC concrete mixes: (a) concrete admixed with only chloride salts, (b) concrete admixed with chloride salts and 3% NaNO₂, and (c) concrete admixed with chloride salts and 3% DHP

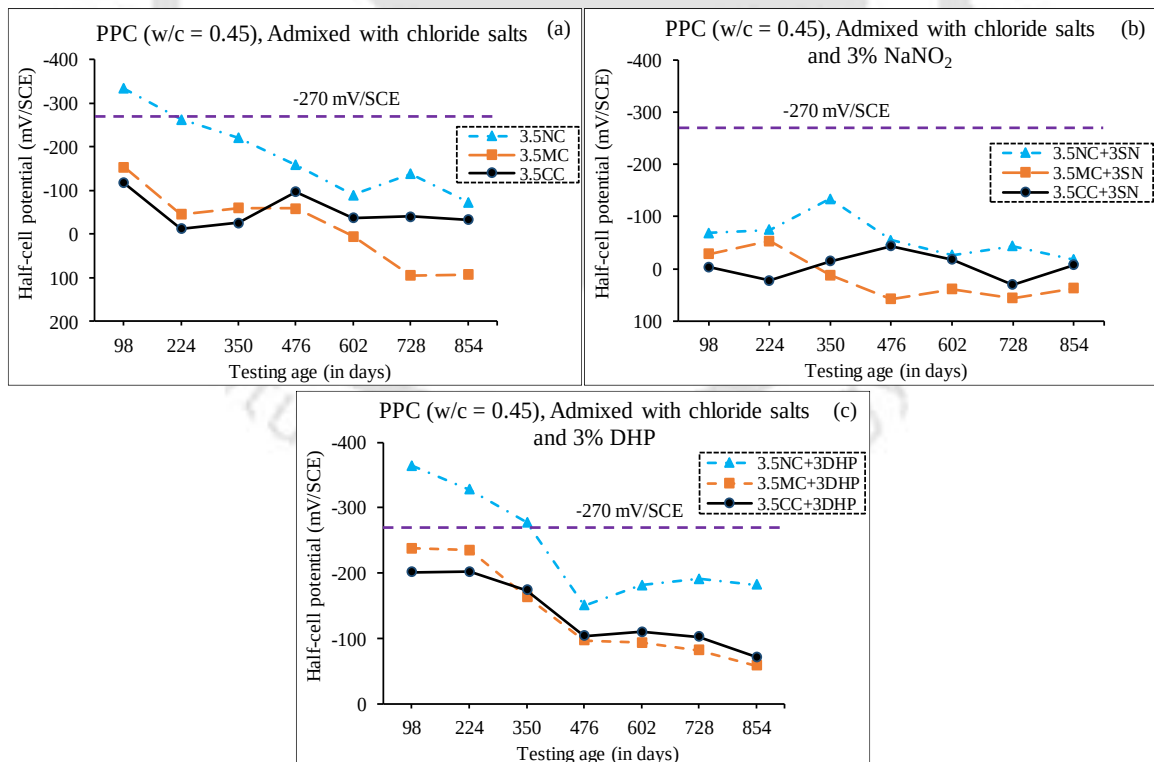


Fig. 5.22 Half-cell potential of reinforcing steel in PPC concrete mixes: (a) concrete admixed with only chloride salts, (b) concrete admixed with chloride salt and 3% NaNO₂, and (c) concrete admixed with chloride salt and 3% DHP

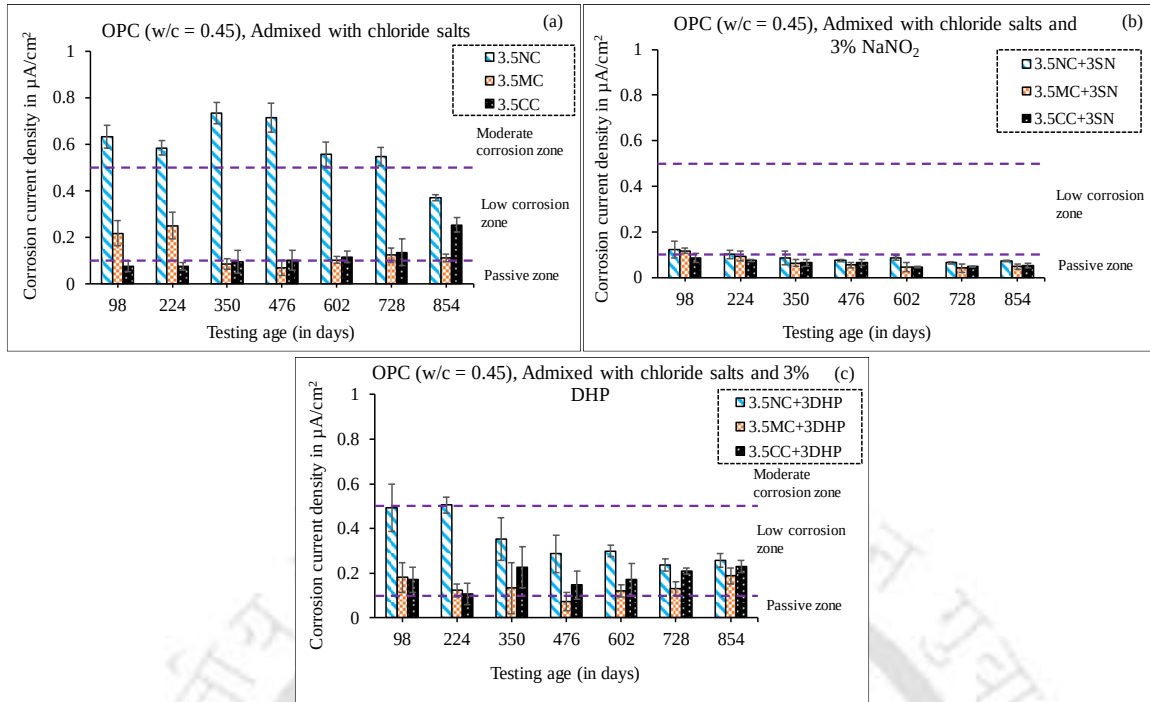


Fig. 5.23 Corrosion current density of reinforcing steel in OPC concrete mixes: (a) concrete admixed with only chloride salts, (b) concrete admixed with chloride salts and 3% $NaNO_2$, and (c) concrete admixed with chloride salts and 3% DHP

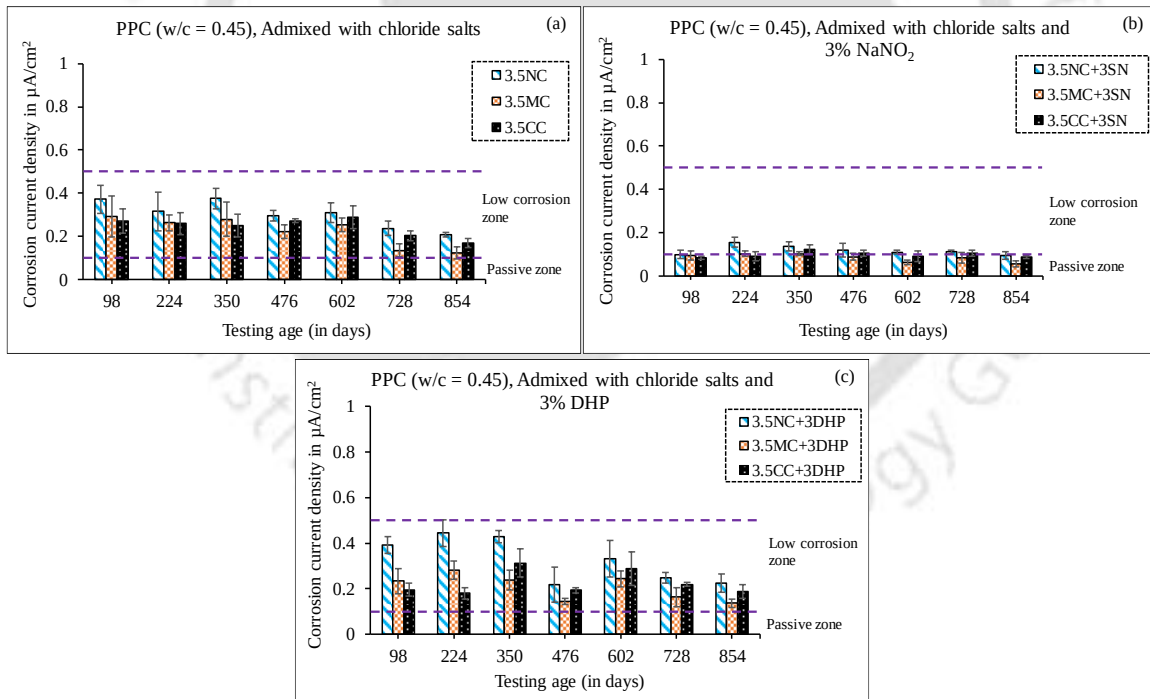


Fig. 5.24 Corrosion current density of reinforcing steel in PPC concrete mixes: (a) concrete admixed with only chloride salts, (b) concrete admixed with chloride salts and 3% $NaNO_2$, and (c) concrete admixed with chloride salts and 3% DHP

From Fig. 5.23 and Fig. 5.24, it is observed that at all ages, the obtained corrosion current density (I_{corr}) of steel reinforcement in cylindrical reinforced concrete specimens was mostly lower than $0.5 \mu A/cm^2$ irrespective of cement type, chloride salt, and presence of

corrosion inhibitors. Although, the chloride ions were present in the concrete from the beginning as chloride salts were added during the preparation of concrete mixes, the effect of unavailability of adequate amount of moisture and variations in oxygen level near steel reinforcement in concrete might have affected the corrosion process of steel reinforcement as indicated by less negative half-cell potential and lower corrosion current density in both OPC and PPC concrete mixes. It may be noted that the cylindrical reinforced concrete specimens were subjected to ambient laboratory dry condition during the exposure period. Although, the corrosion activity of steel reinforcement in concrete was lower, the addition of NaNO_2 in chloride contaminated concrete resulted in comparatively less negative half-cell potential (E_0) and lower corrosion current density (I_{corr}) as compared to that admixed with only chloride salt at all ages irrespective of cement type, and chloride salt. This may be due to the effect of formation of stable passive film of Fe_2O_3 over steel surface due to oxidization of iron by nitrite ions that inhibited the steel rebar [183]. In the process of oxidization of iron, the preferential reaction of nitrite ions than chloride ions with ferrous ions results in the formation of ferric oxide [18, 85, 184]. Further, at the age of 854 days, the obtained free chloride content near rebar level was also slightly lower in the concrete mixes admixed with chloride salt plus NaNO_2 than that admixed with only chloride salt. The half-cell potential values of rebar were mostly more negative and corrosion current density values were comparatively higher in the mixes admixed with chloride salt plus DHP than that admixed with only chloride salt at all ages as observed from Fig. 5.21 to Fig. 5.24. It may be noted that the free chloride content near rebar level was slightly lower in the mixes containing chloride salt plus DHP as compared to that admixed with only chloride salt. Thus, relatively higher extent of corrosion activity of steel reinforcement in the concrete mixes added with chloride salt plus DHP may be ascribed to the dominant effect of alteration in oxygen and moisture content near rebar level over the effect of slightly lower free chloride content in the concrete mixes added with chloride salt plus DHP. While comparing the corrosion inhibitor, it is inferred that the E_0 was less negative, and I_{corr} was lower in the presence of NaNO_2 than that in the presence of DHP irrespective of cement type and chloride salt as noted from Fig. 5.21 to Fig. 5.24. Although the extent of corrosion activity was lower, the better performance of NaNO_2 against steel reinforcement corrosion in comparison to DHP may be due to the ability of nitrite ions to repel the chloride ions from the surface of steel reinforcement and formation of more stable passive layer over the steel surface than that in case of DHP. In addition, in case of DHP, the phosphate ions react with calcium ions and form calcium phosphate, which reduces the availability of

phosphates ions thereby partially decreasing the inhibiting efficiency of di-Sodium hydrogen phosphate [130].

From Fig. 5.21 to Fig. 5.24, it is inferred that the half-cell potential (E_0) was comparatively more negative and corrosion current density (I_{corr}) was comparatively higher in the concrete admixed with NaCl than that admixed with CaCl_2 , and MgCl_2 for both cements and both corrosion inhibitors. This may be ascribed to the effect of presence of higher free chloride content near steel bar in the concrete containing NaCl, although the extent of corrosion activity of steel reinforcement in the concrete was lower irrespective of chloride salt. As stated earlier, at the age of 854 days, the free chloride content near steel bar was higher in the concrete containing NaCl as compared to CaCl_2 , and MgCl_2 . Between MgCl_2 and CaCl_2 , initially i.e., during early age till about 224 days, the half-cell potential (E_0) was more negative and corrosion current density (I_{corr}) was higher in the concrete admixed with MgCl_2 as compared to that admixed with CaCl_2 for both cements and both corrosion inhibitors. However, during later age i.e. after 224 days, the half-cell potential became more negative and corrosion current density of steel reinforcement was higher in the concrete admixed with CaCl_2 as compared to MgCl_2 . During early age, the more negative E_0 and higher I_{corr} of rebar in concrete admixed with MgCl_2 as compared to CaCl_2 may be attributed to the dominant effect of formation of higher amount of calcium hypochlorite in the presence of MgCl_2 that causes a decrease in the alkalinity of concrete, and lower chloride binding capacity of concrete due to formation of magnesium hydroxide ($\text{Mg}(\text{OH})_2$) and magnesium silicate hydrate (M-S-H) in the presence of MgCl_2 in the concrete [52]. However, during later age, the more negative half-cell potential and higher corrosion current density of steel bar in the concrete admixed with CaCl_2 as compared to MgCl_2 may be attributed to the significant effect of higher free chloride content in the concrete admixed with CaCl_2 than MgCl_2 although, the alkalinity and chloride binding were higher in the concrete admixed with CaCl_2 .

From Fig. 5.21 and Fig. 5.22, it is observed that in case of concrete mixes added with chloride salt and those added with chloride salt plus DHP, the specimens prepared from PPC mostly showed more negative half-cell potential as compared to those prepared from OPC irrespective of admixed chloride salt at all ages. However, in case of mixes added with chloride salt plus NaNO_2 , OPC specimens mostly showed more negative half-cell potential than PPC specimens. Further, OPC concrete showed better performance against corrosion of steel reinforcement as compared to PPC concrete as indicated by the corrosion

current density values shown in Fig. 5.23 and Fig. 5.24, where OPC concrete mostly showed lower corrosion current density as compared to PPC concrete irrespective of admixed chloride salts and corrosion inhibitors at all ages. This may be attributed to the presence of lower amount of free chloride and higher amount of bound chloride in OPC concrete mixes than that in PPC concrete mixes. It may be noted that at the age of 854 days, the bound chloride content was higher, and free chloride content was lower near steel reinforcement (Table 5.1) in OPC concrete mixes as compared to that in PPC concrete mixes. The half-cell potential mostly became less negative, and corrosion current density mostly decreased with age irrespective of cement type, admixed chloride salt, and corrosion inhibitor as observed from Fig. 5.21 to Fig. 5.24. The reason behind this may be attributed to the dominant effect of alterations in oxygen level, and moisture content near rebar level in concrete.

5.5 Summary

From the obtained results, it is observed that the use of NaNO_2 and DHP in chloride contaminated concrete increased the binding of chloride ions thereby reducing the availability of free chloride near steel bar irrespective of cement type and admixed chloride salts. These results were further confirmed with the results of XRD and FESEM analyses of concrete mixes, which showed formation of more amount of calcium chloroaluminate (Friedel's salt) in the concrete admixed with chloride salt plus corrosion inhibitor than that admixed with only chloride salt. Further, the bound chloride content was higher in DHP added concrete mixes than NaNO_2 added concrete mixes. The concrete admixed with NaCl showed higher free chloride ion content and lower bound chloride content as compared to CaCl_2 and MgCl_2 . The XRD analysis indicated the formation of higher amount of calcium hypochlorite in the concrete added with MgCl_2 than that added with CaCl_2 . Further, the formation of calcium chloroaluminate was more in CaCl_2 added concrete mixes than MgCl_2 and NaCl added concrete mixes. The results of electrochemical tests indicated lower probability of occurrence of steel bar corrosion and lower corrosion current density in the concrete contaminated with chloride salts irrespective of cement type, cation type of chloride salt, and corrosion inhibitors. Even though the extent of corrosion was lower, the addition of sodium nitrite in chloride contaminated concrete showed comparatively less negative half-cell potential (E_0) and lower corrosion current density (I_{corr}) as compared to the concrete admixed with only chloride salt. However, in most of the concrete mixes, DHP added specimens in the presence of chloride ions showed comparatively more negative

half-cell potential and higher corrosion current density as compared to those added with only chloride salt. The concrete mixes added with NaCl showed more negative half-cell potential as well as higher corrosion current density than those added with CaCl_2 and MgCl_2 irrespective of cement type and corrosion inhibitor. Between cement type, the OPC concrete mixes showed better performance against steel reinforcement corrosion as compared to PPC mixes irrespective of chloride salts and corrosion inhibitors.



Influence of Corrosion Inhibitors on Rebar Corrosion in Concrete Subjected to Chloride and Composite Chloride-Sulfate Environment

6.1 General

In this chapter, the results obtained from the experimental study conducted to evaluate the effect of chloride ions associated with different cations on corrosion behaviour of steel reinforcement in concrete containing different corrosion inhibitors are presented, and discussed. The concrete mixes were prepared from OPC, and PPC at w/c of 0.45, and 0.55. The cylindrical reinforced concrete specimens admixed with, and without corrosion inhibitors were subjected to chloride, and composite chloride-sulfate solutions for an exposure period of 819 days. The corrosion behaviour of steel reinforcement in concrete was evaluated through electrochemical measurements such as half-cell potential, and linear polarization resistance (LPR) measurements. From the obtained results of electrochemical measurements, the variations in half-cell potential (E_0), and corrosion current density (I_{corr}) of steel reinforcement in concrete with cement type, w/c, corrosion inhibitor, cation type of chloride salt, exposure solution, and exposure duration are evaluated. Further, the effects of cation type of chloride salts on free chloride ion (C_F), and bound chloride ion (C_B) contents in concrete admixed with, and without corrosion inhibitors, and exposed to different chloride, and composite chloride-sulfate solutions are analyzed, and discussed. In addition, to examine the effect of different chloride salts on changes in microstructure of concrete in the presence of corrosion inhibitors, the results obtained from X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and Field emission scanning electron microscope (FESEM) analyses are also presented, and discussed in this chapter.

6.2 Corrosion parameters

As stated earlier in Chapter 3, the half-cell potential (E_0) test, and corrosion current density (I_{corr}) by linear polarization resistance (LPR) measurement were carried out on the cylindrical specimens at different intervals till the exposure period of 819 days. For a given concrete mix, and exposure solution, the corrosion tests were performed on three replicate cylindrical specimens, and the average value was reported. From the obtained E_0 values, the probability of occurrence of steel reinforcement corrosion in concrete was evaluated based on the criteria mentioned in ASTM C876-15 [182]. The average E_0 of steel reinforcement in cylindrical specimens made from OPC, and PPC at w/c of 0.45, and 0.55;

admixed with, and without corrosion inhibitors; and exposed to chloride (3.5% NaCl, 3.5% MgCl_2 , and 3.5% CaCl_2), and composite chloride-sulfate solutions (3.5% NaCl+3.5% MgSO_4 , 3.5% MgCl_2 +3.5% MgSO_4 , and 3.5% CaCl_2 +3.5% MgSO_4) are shown in Fig. 6.1 to Fig. 6.6.

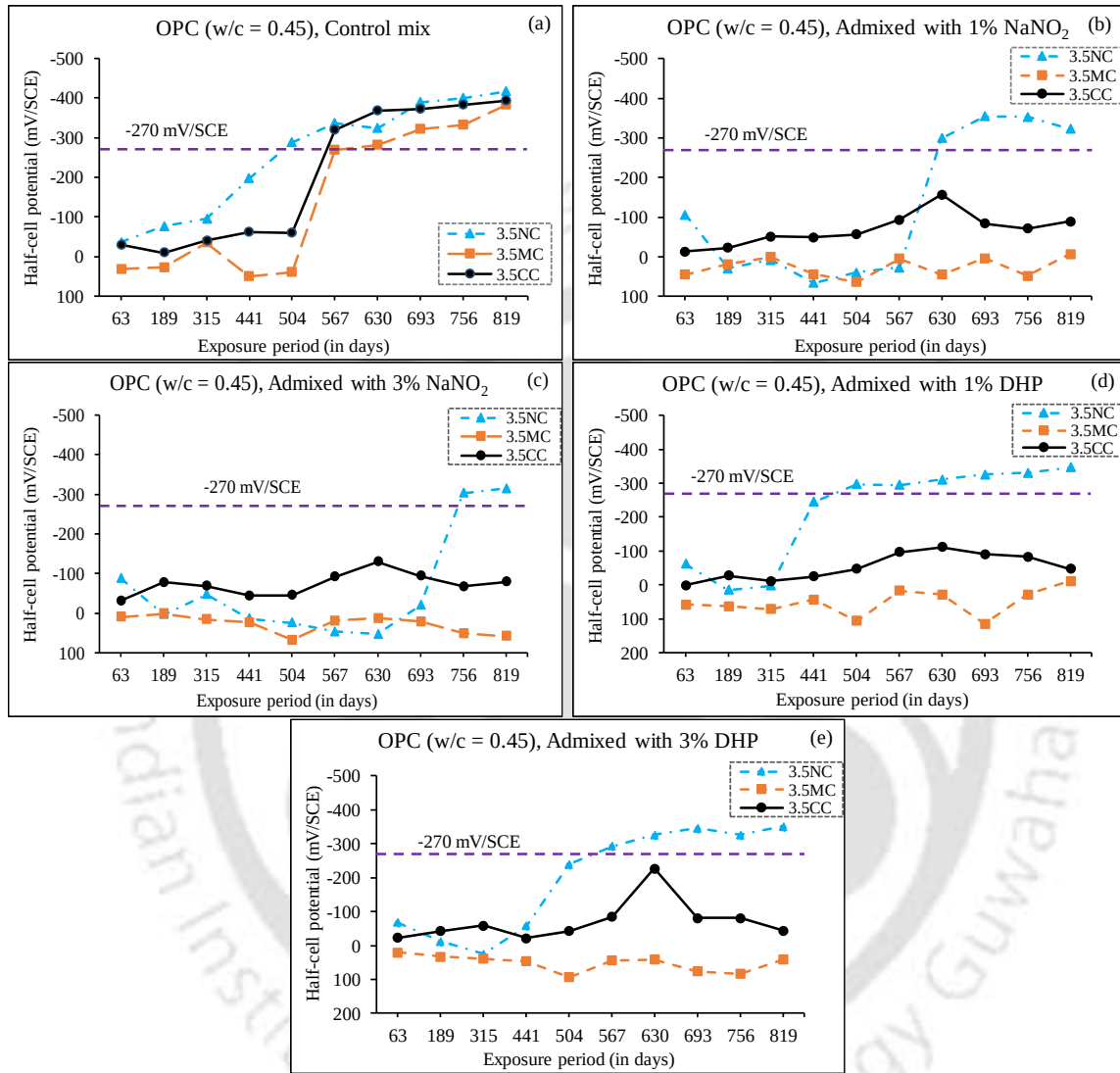


Fig. 6.1 Half-cell potential (E_0) of steel reinforcement in OPC concrete at w/c of 0.45, and exposed to 3.5% chloride salt solutions (i.e., NaCl, MgCl_2 , and CaCl_2): (a) control mix, (b) concrete admixed with 1% NaNO_2 , (c) concrete admixed with 3% NaNO_2 , (d) concrete admixed with 1% DHP, and (e) concrete admixed with 3% DHP

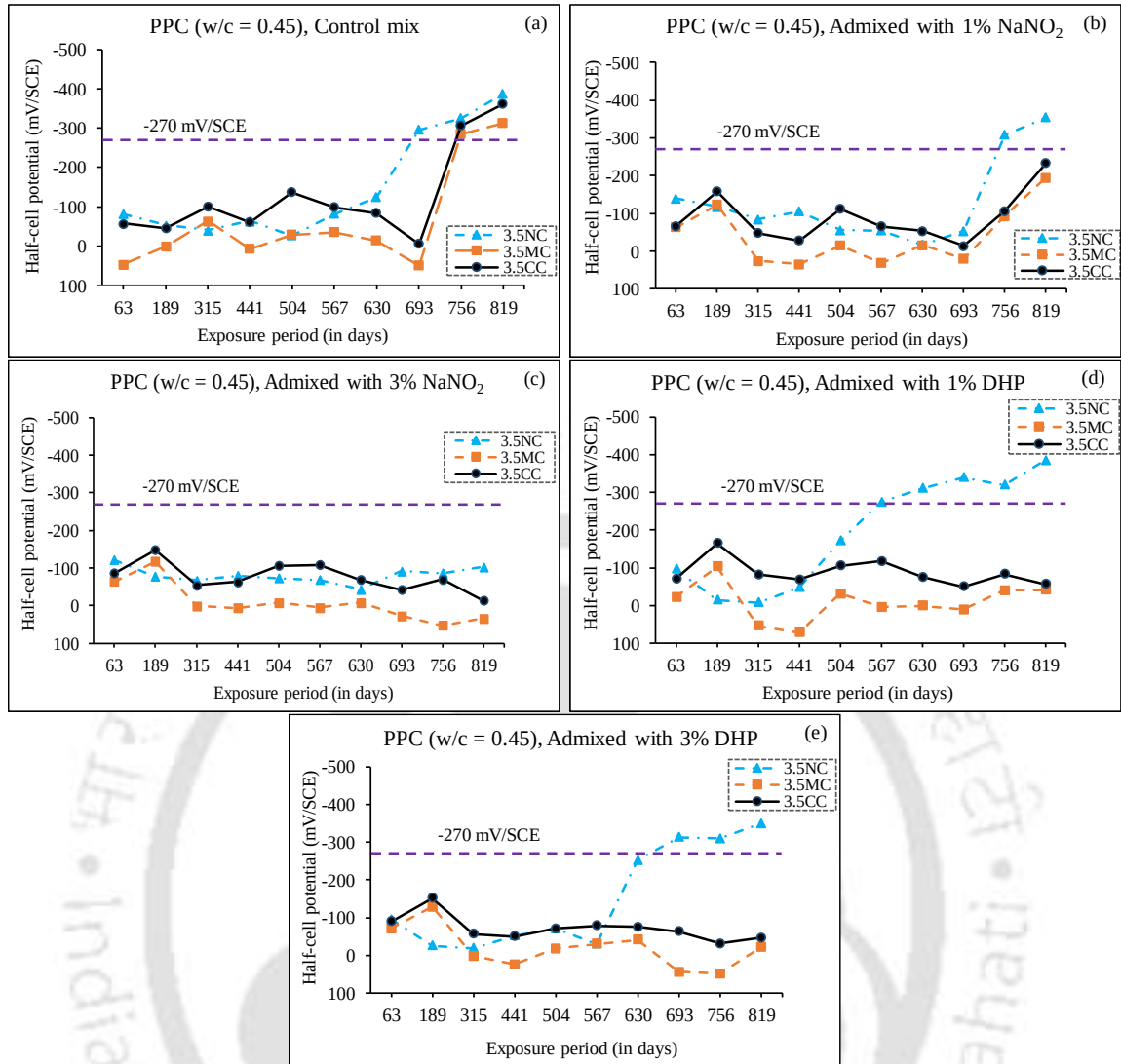
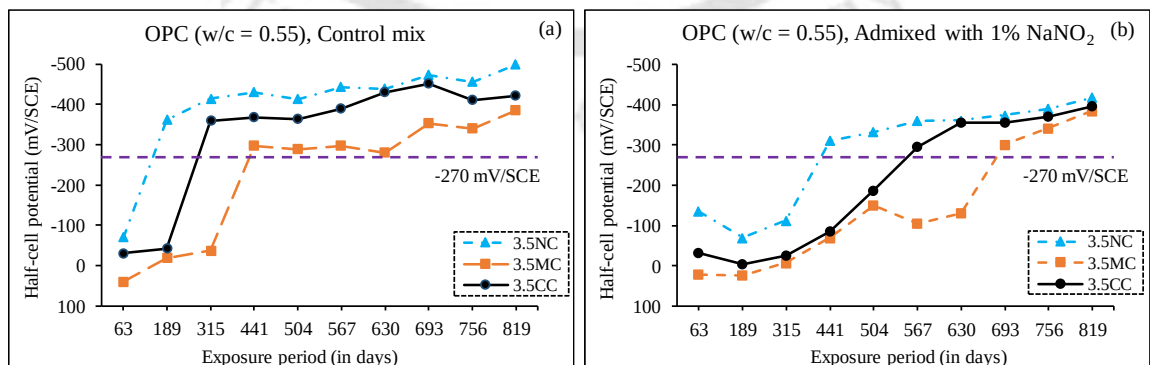


Fig. 6.2 Half-cell potential (E_0) of steel reinforcement in PPC concrete at w/c of 0.45, and exposed to 3.5% chloride salt solutions (i.e., $NaCl$, $MgCl_2$, and $CaCl_2$): (a) control mix, (b) concrete admixed with 1% $NaNO_2$, (c) concrete admixed with 3% $NaNO_2$, (d) concrete admixed with 1% DHP, and (e) concrete admixed with 3% DHP



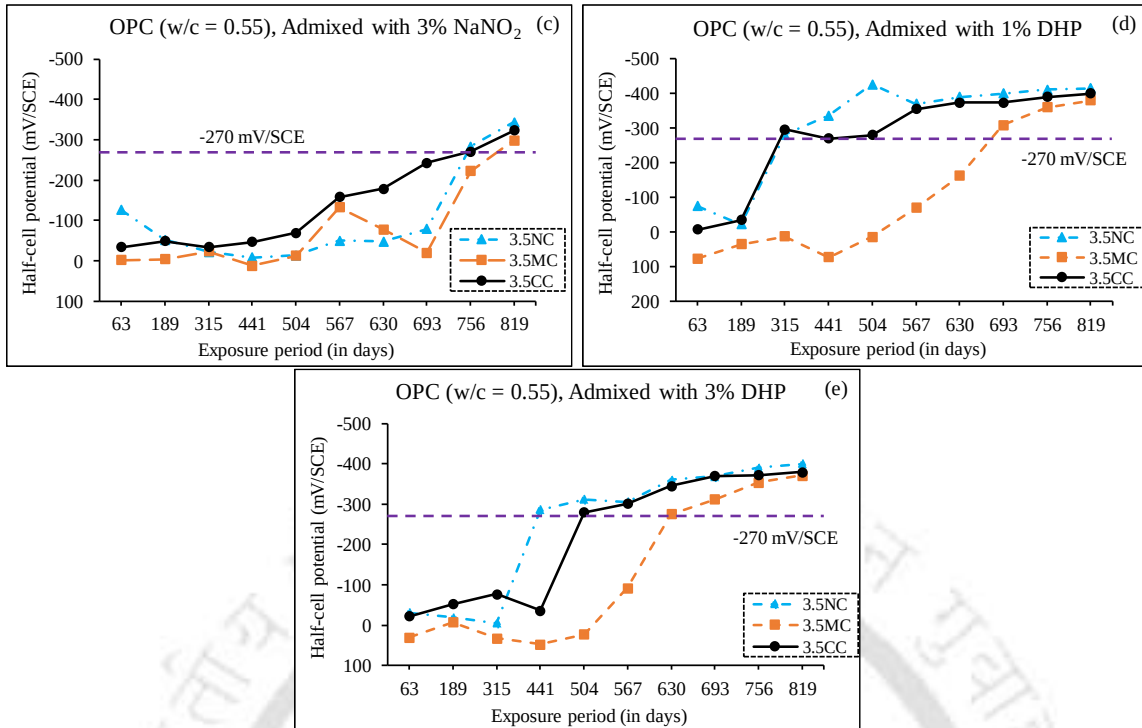
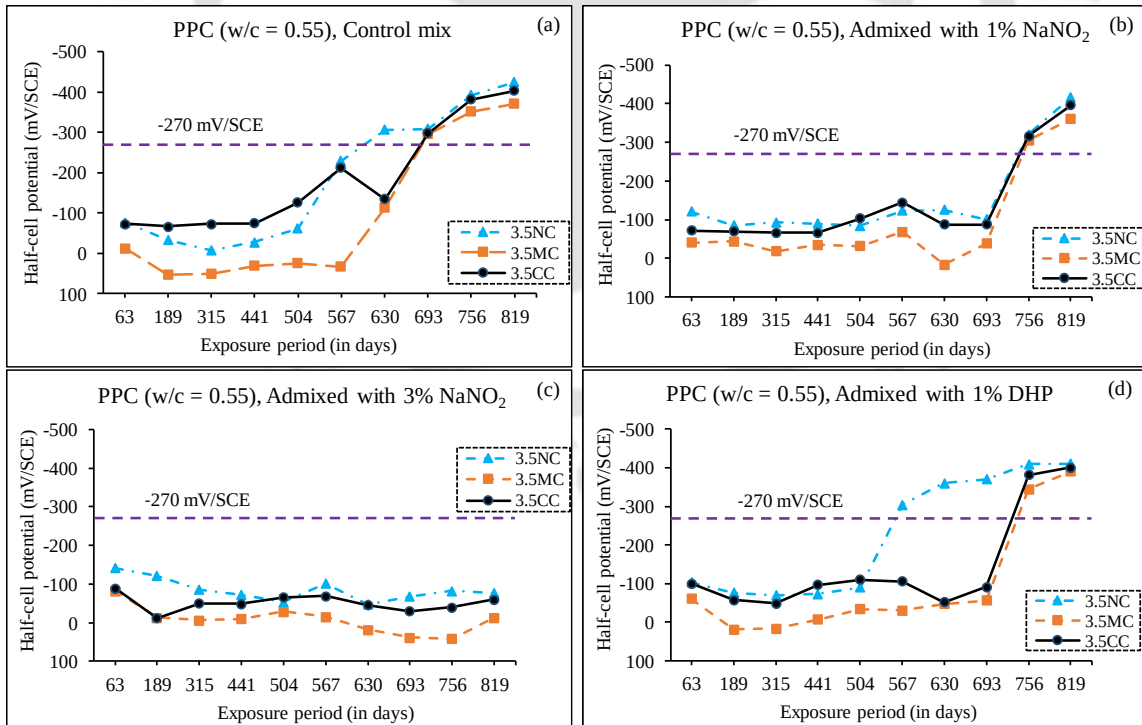


Fig. 6.3 Half-cell potential (E_0) of steel reinforcement in OPC concrete at w/c of 0.55, and exposed to 3.5% chloride salt solutions (i.e., NaCl, $MgCl_2$, and $CaCl_2$): (a) control mix, (b) concrete admixed with 1% $NaNO_2$, (c) concrete admixed with 3% $NaNO_2$, (d) concrete admixed with 1% DHP, and (e) concrete admixed with 3% DHP



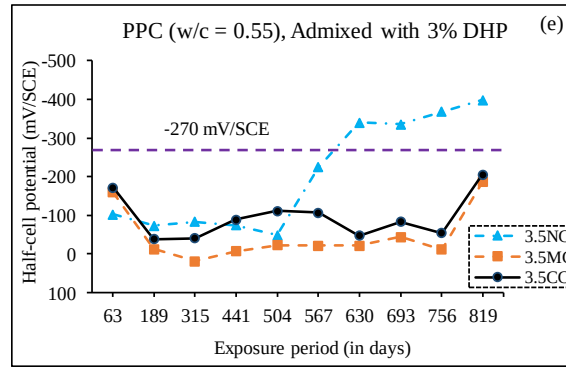


Fig. 6.4 Half-cell potential (E_0) of steel reinforcement in PPC concrete at w/c of 0.55, and exposed to 3.5% chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂): (a) control mix, (b) concrete admixed with 1% NaNO₂, (c) concrete admixed with 3% NaNO₂, (d) concrete admixed with 1% DHP, and (e) concrete admixed with 3% DHP

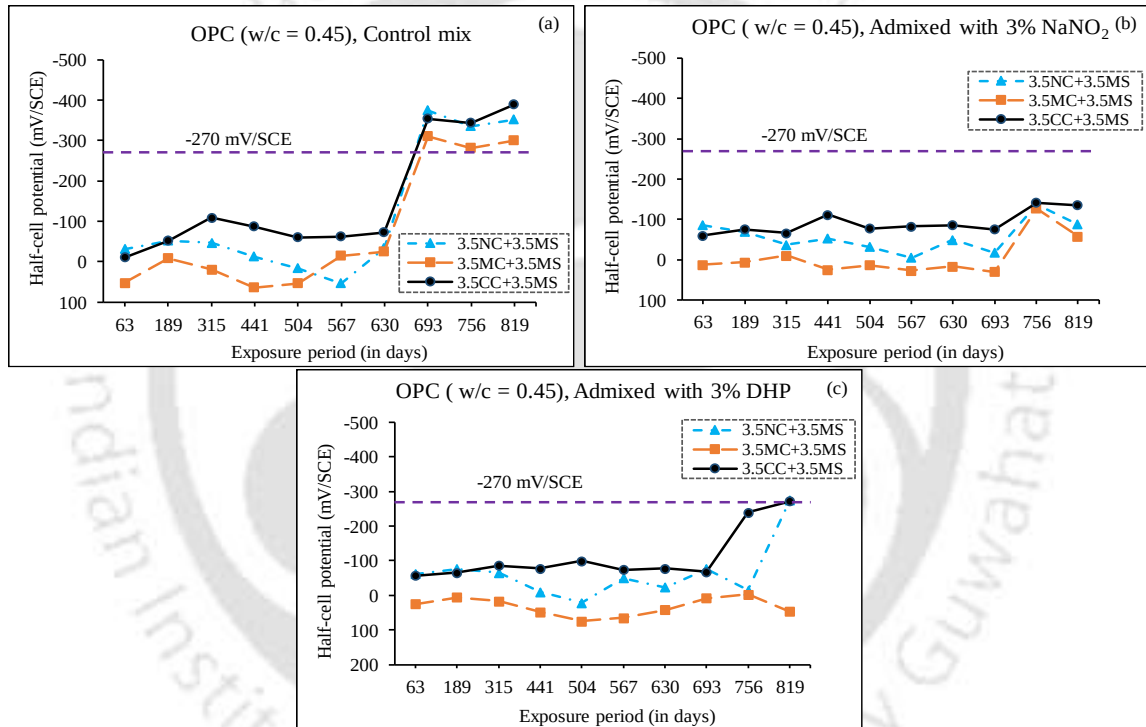
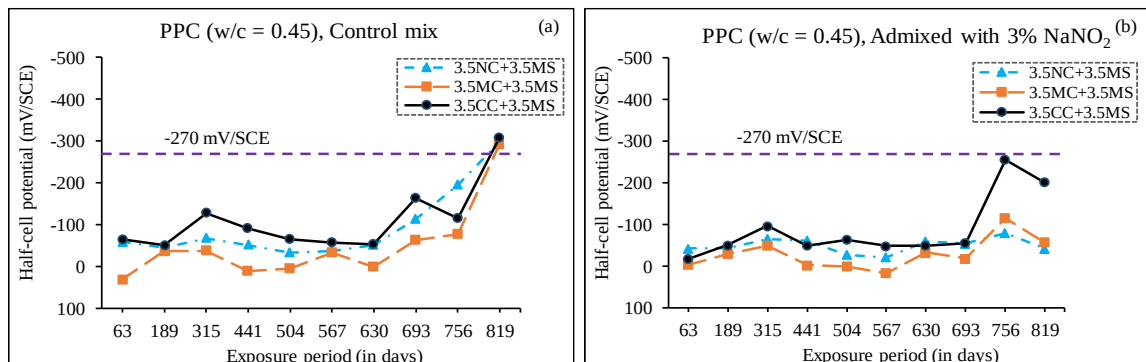


Fig. 6.5 Half-cell potential (E_0) of steel reinforcement in OPC concrete at w/c of 0.45, and exposed to composite chloride-sulfate solutions: (a) control mix, (b) concrete admixed with 3% NaNO₂, and (c) concrete admixed with 3% DHP



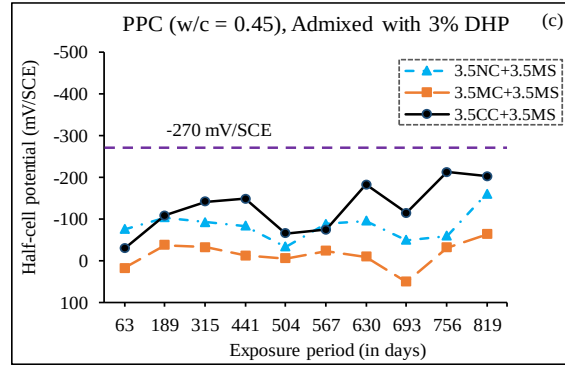
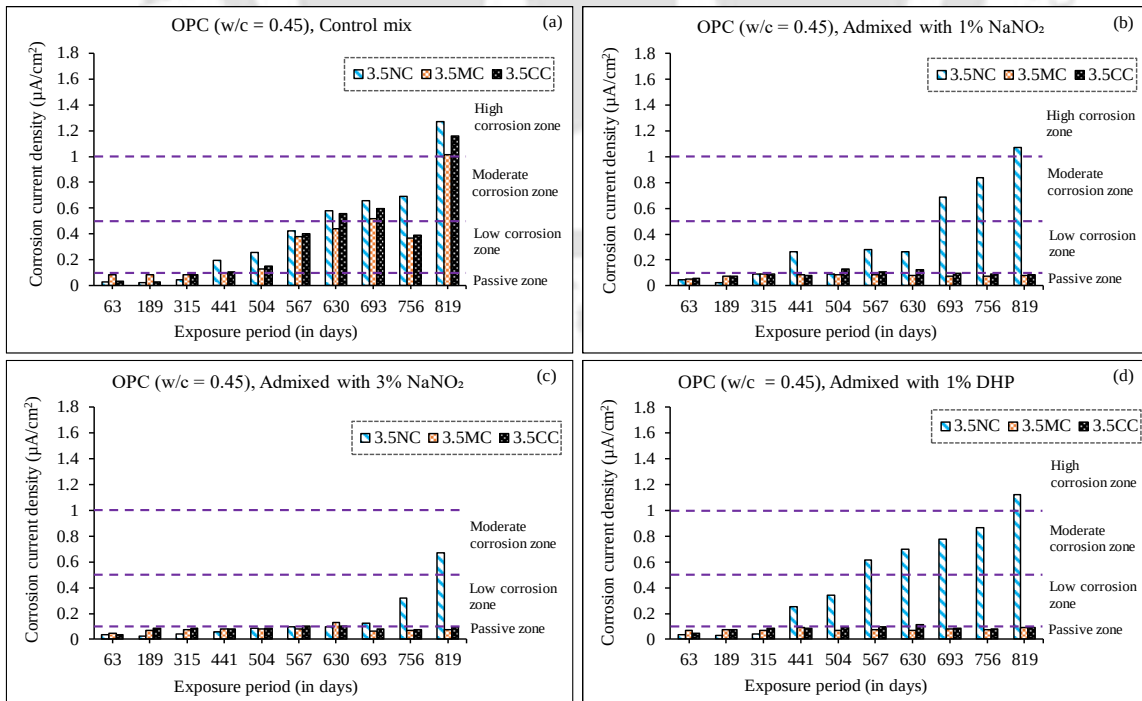


Fig. 6.6 Half-cell potential (E_0) of steel reinforcement in PPC concrete at w/c of 0.45, and exposed to composite chloride-sulfate solutions: (a) control mix, (b) concrete admixed with 3% NaNO_2 , and (c) concrete admixed with 3% DHP

The average I_{corr} of steel reinforcement in cylindrical specimens prepared from OPC, and PPC at w/c of 0.45, and 0.55; admixed with, and without corrosion inhibitors, and exposed to chloride (3.5% NaCl , 3.5% MgCl_2 , and 3.5% CaCl_2), and composite chloride-sulfate solutions (3.5% NaCl +3.5% MgSO_4 , 3.5% MgCl_2 +3.5% MgSO_4 , and 3.5% CaCl_2 +3.5% MgSO_4) are shown in Fig. 6.7 to Fig. 6.12. On the basis of obtained values of I_{corr} , the corrosion level of steel reinforcement in concrete was divided into four zones namely passive zone (I_{corr} : less than $0.1 \mu\text{A}/\text{cm}^2$), low corrosion zone (I_{corr} : 0.1 to $0.5 \mu\text{A}/\text{cm}^2$), moderate corrosion zone (I_{corr} : 0.5 to $1.0 \mu\text{A}/\text{cm}^2$), and high corrosion zone (I_{corr} : greater than $1 \mu\text{A}/\text{cm}^2$) [185, 186]. These zones with respect to I_{corr} are shown in Fig. 6.7 to Fig. 6.12.



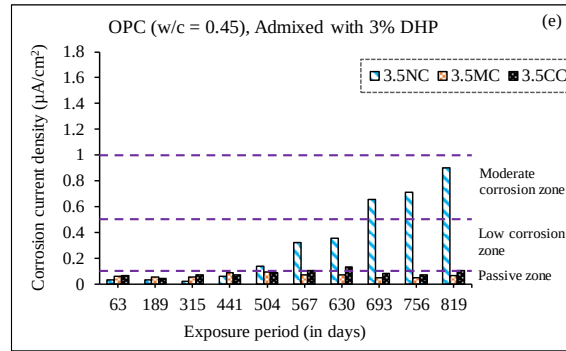


Fig. 6.7 Corrosion current density (I_{corr}) of steel reinforcement in OPC concrete at w/c of 0.45, and exposed to 3.5% chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂): (a) control mix, (b) concrete admixed with 1% NaNO₂, (c) concrete admixed with 3% NaNO₂, (d) concrete admixed with 1% DHP, and (e) concrete admixed with 3% DHP

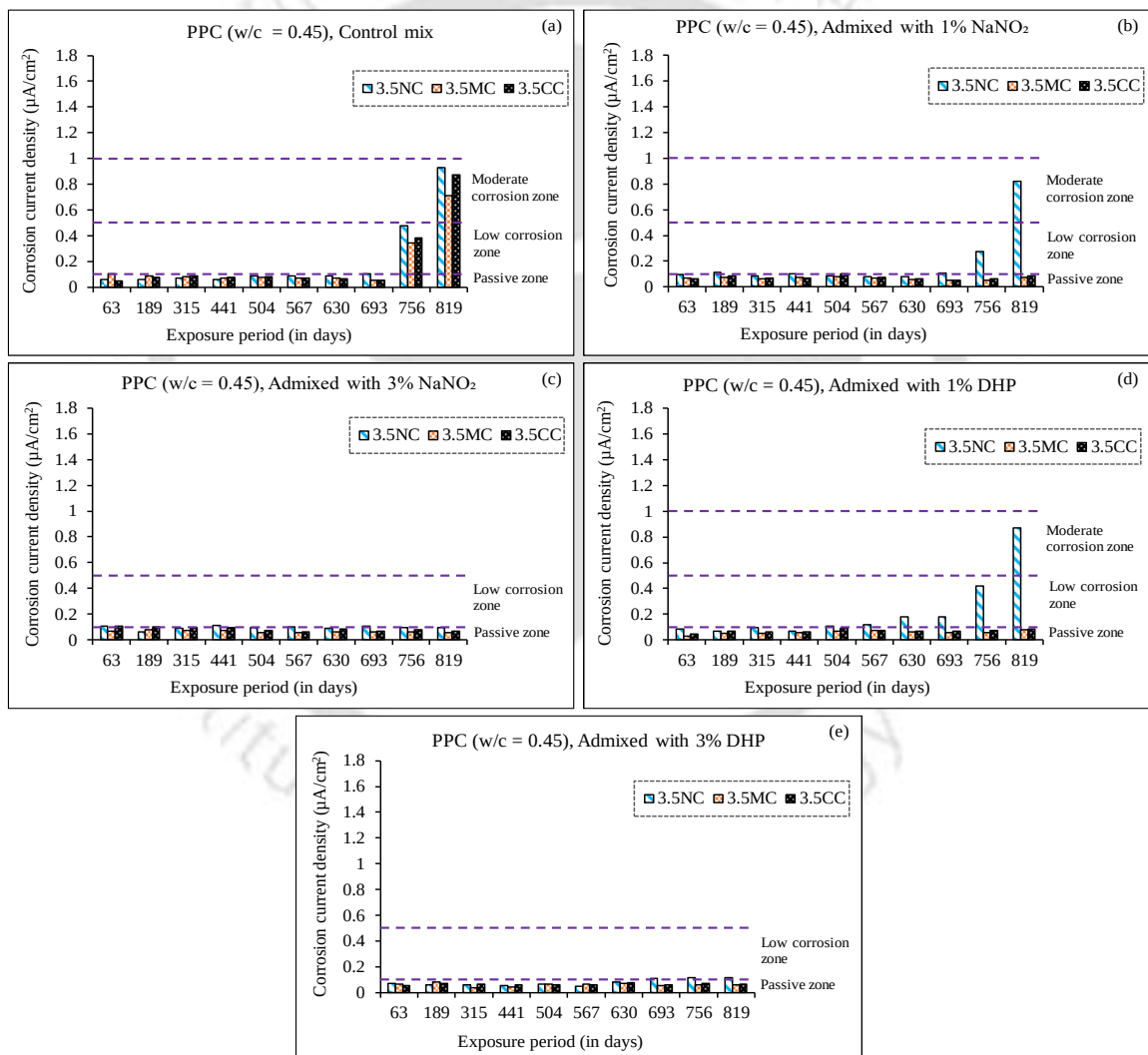


Fig. 6.8 Corrosion current density (I_{corr}) of steel reinforcement in PPC concrete at w/c of 0.45, and exposed to 3.5% chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂): (a) control mix, (b) concrete admixed with 1% NaNO₂, (c) concrete admixed with 3% NaNO₂, (d) concrete admixed with 1% DHP, and (e) concrete admixed with 3% DHP

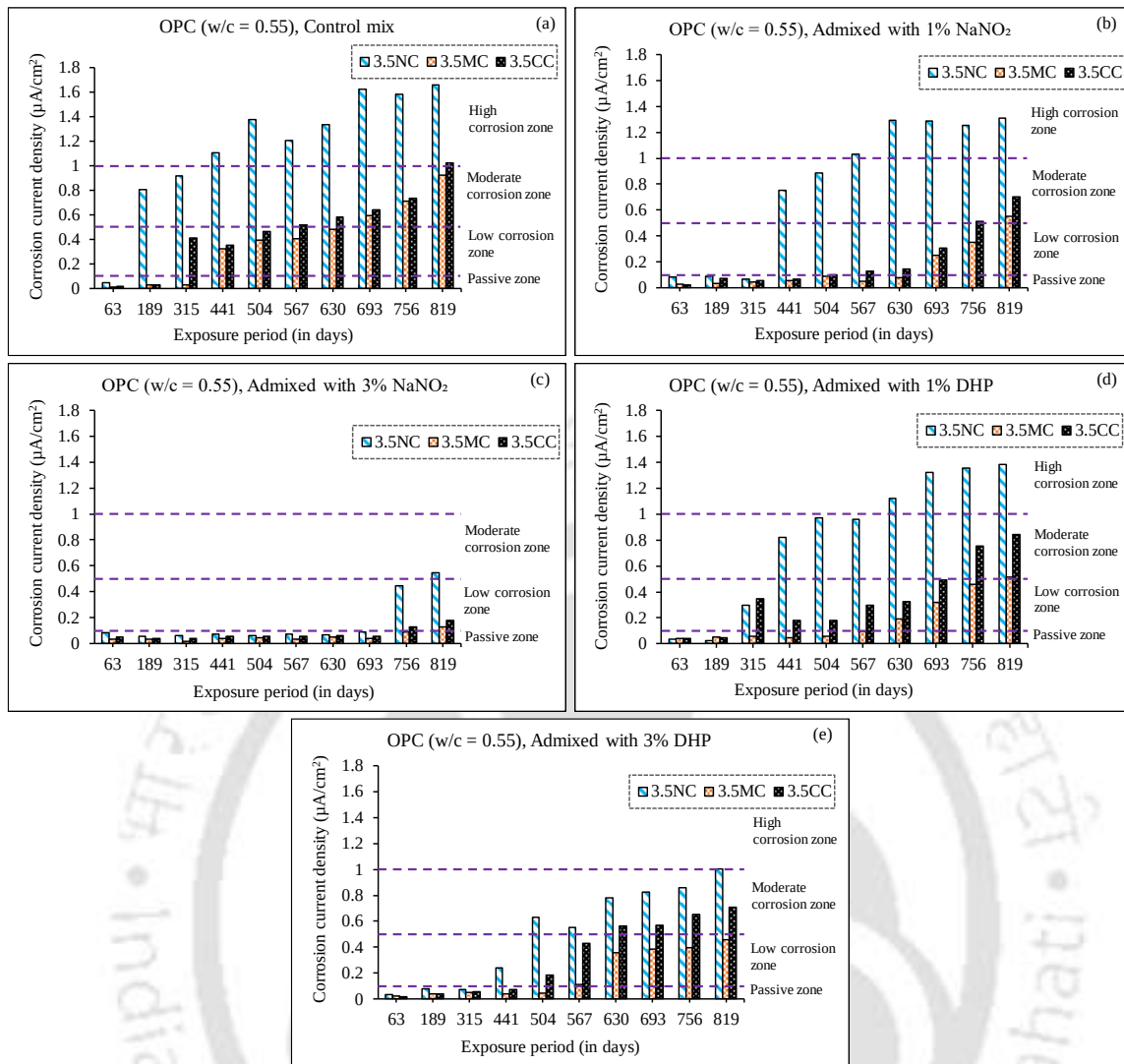
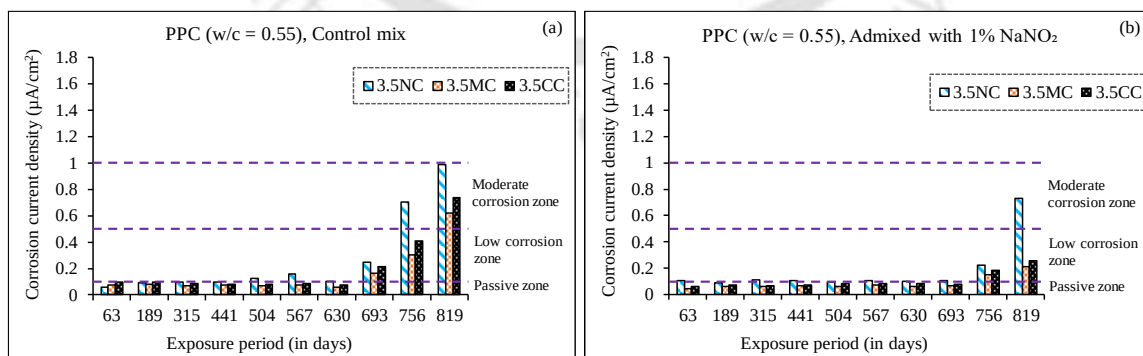


Fig. 6.9 Corrosion current density (I_{corr}) of steel reinforcement in OPC concrete at w/c of 0.55, and exposed to 3.5% chloride salt solutions (i.e., $NaCl$, $MgCl_2$, and $CaCl_2$): (a) control mix, (b) concrete admixed with 1% $NaNO_2$, (c) concrete admixed with 3% $NaNO_2$, (d) concrete admixed with 1% DHP, and (e) concrete admixed with 3% DHP



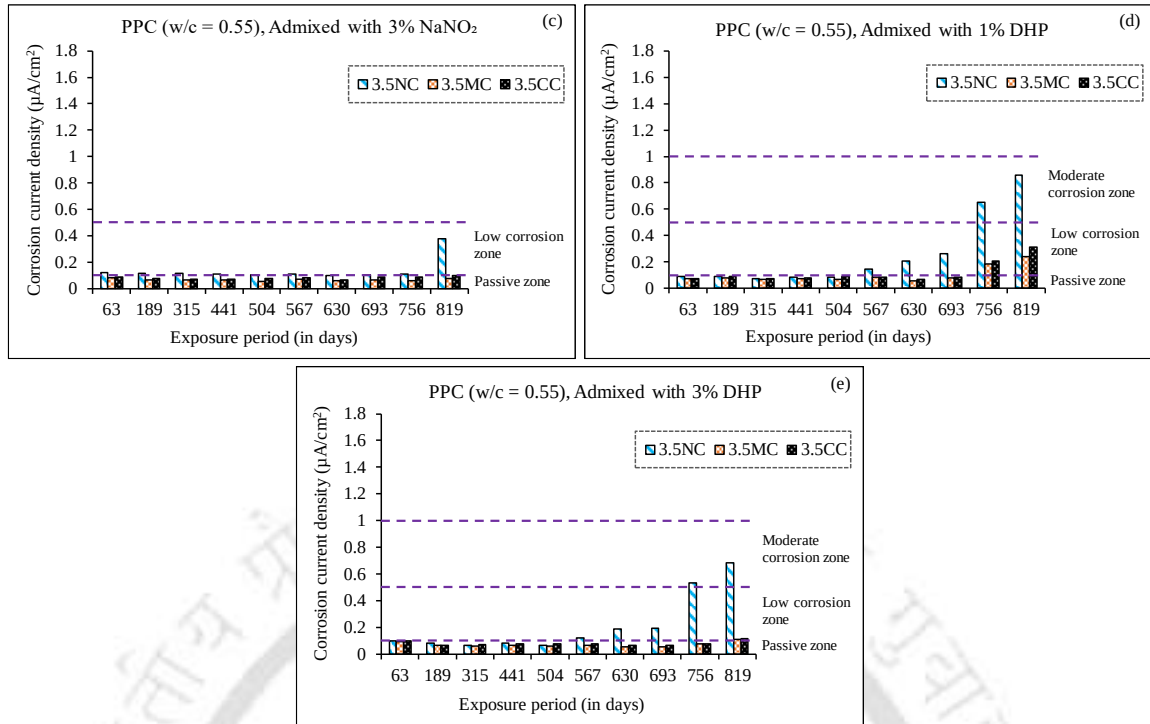


Fig. 6.10 Corrosion current density (I_{corr}) of steel reinforcement in PPC concrete at w/c of 0.55, and exposed to 3.5% chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂): (a) control mix, (b) concrete admixed with 1% NaNO₂, (c) concrete admixed with 3% NaNO₂, (d) concrete admixed with 1% DHP, and (e) concrete admixed with 3% DHP

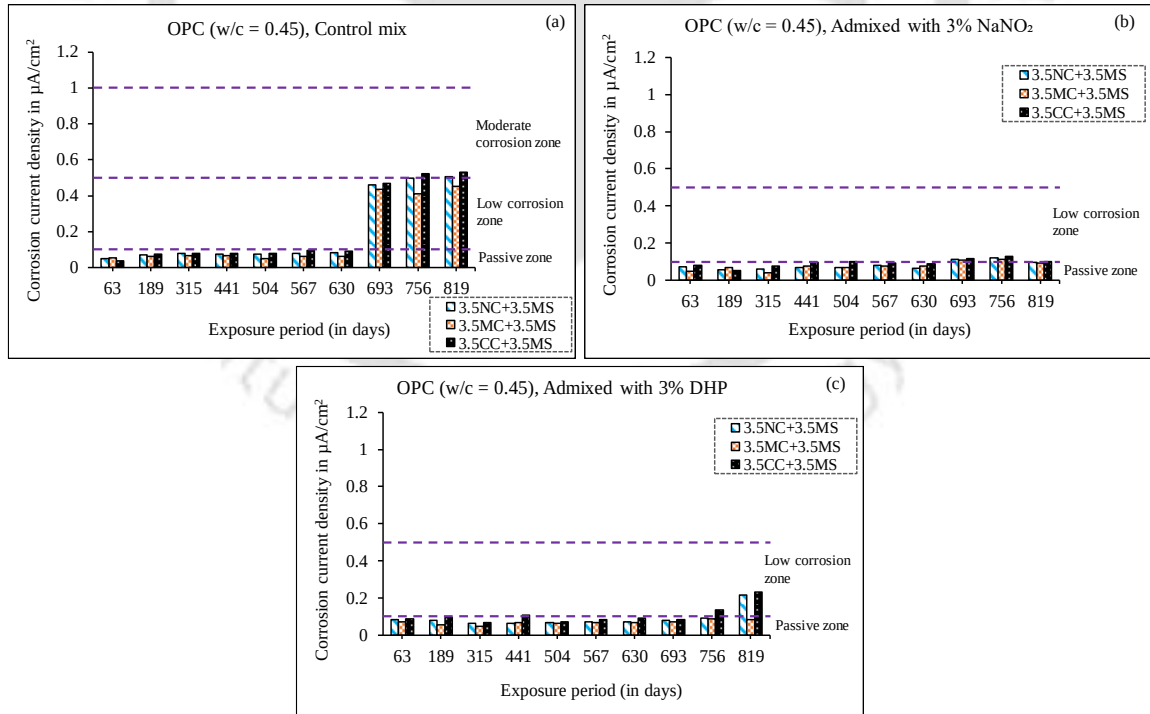


Fig. 6.11 Corrosion current density (I_{corr}) of steel reinforcement in OPC concrete at w/c of 0.45, and exposed to composite chloride-sulfate solutions: (a) control mix, (b) concrete admixed with 3% NaNO₂, and (c) concrete admixed with 3% DHP

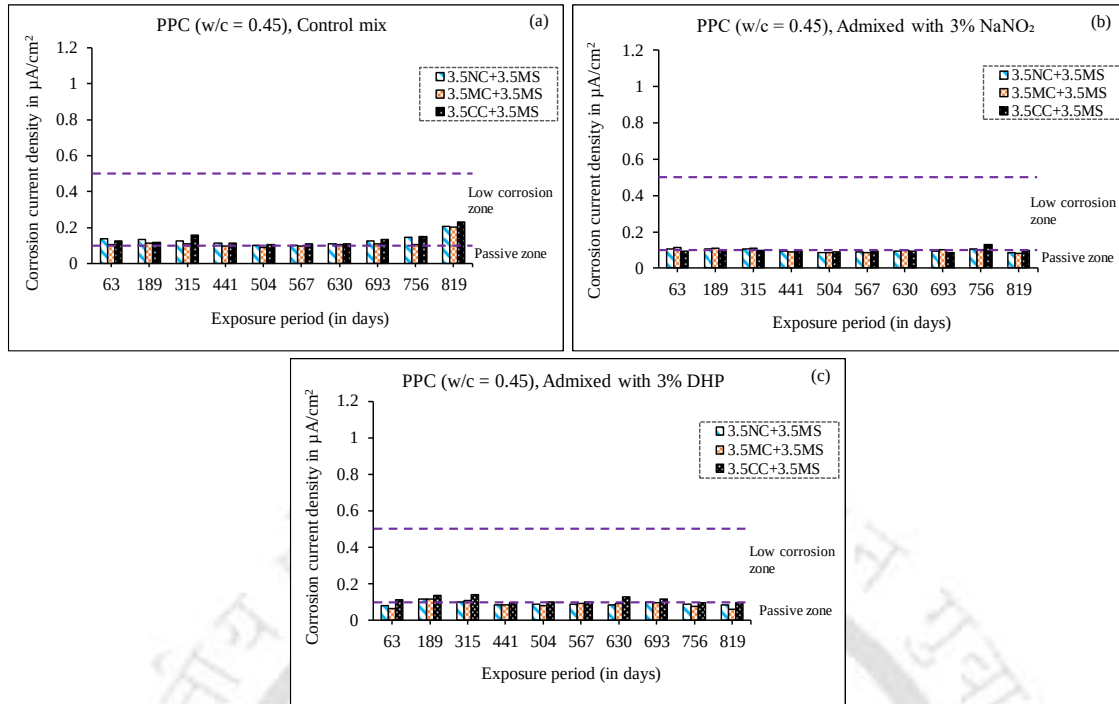


Fig. 6.12 Corrosion current density (I_{corr}) of steel reinforcement in PPC concrete at w/c of 0.45, and exposed to composite chloride-sulfate solutions: (a) control mix, (b) concrete admixed with 3% NaNO_2 , and (c) concrete admixed with 3% DHP

As already stated in Chapter 3, in case of external exposure, the cylindrical specimens were exposed to sodium chloride solutions of different concentrations such as 1.5%, 3.5%, and 5.5% to investigate the effect of chloride concentration on half-cell potential, and corrosion current density of steel reinforcement in concrete. The plots of average E_0 , and I_{corr} of steel reinforcement in cylindrical specimens made from OPC, and PPC at w/c of 0.45, and 0.55; admixed with, and without corrosion inhibitors, and exposed to 1.5% NaCl, and 5.5% NaCl solutions are shown in Appendix A: Fig. A1 to Fig. A8. Typical plots of average E_0 , and I_{corr} of steel reinforcement for all concentrations of NaCl are shown in Fig. 6.13 to Fig. 6.16.

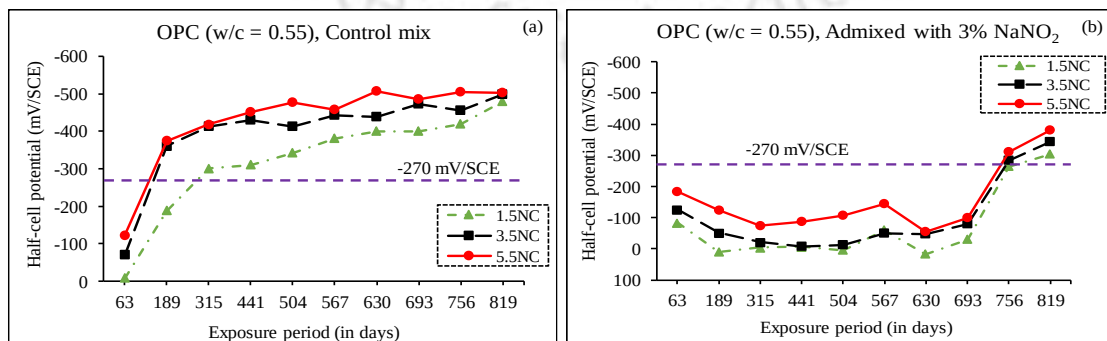


Fig. 6.13 Half-cell potential (E_0) of steel reinforcement in OPC concrete at w/c of 0.55, and exposed to different concentrations of NaCl solution: (a) control mix, and (b) concrete admixed with 3% NaNO_2

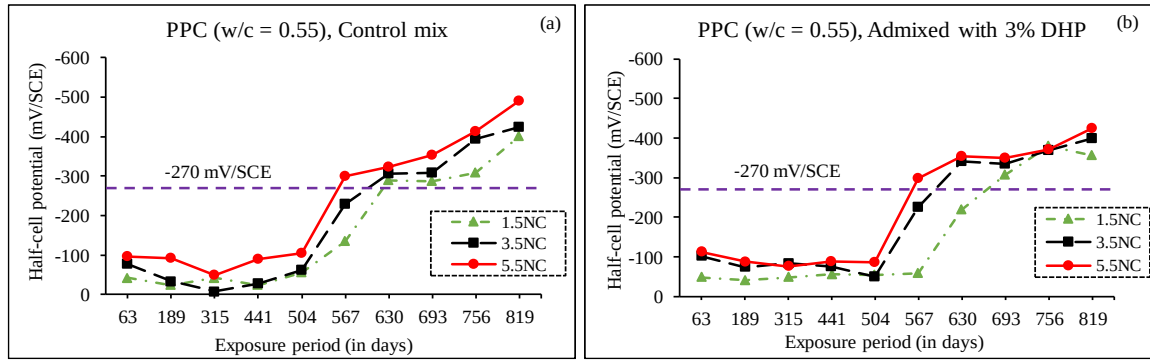


Fig. 6.14 Half-cell potential (E_0) of steel reinforcement in PPC concrete at w/c of 0.55, and exposed to different concentrations of NaCl solution: (a) control mix, and (b) concrete admixed with 3% DHP

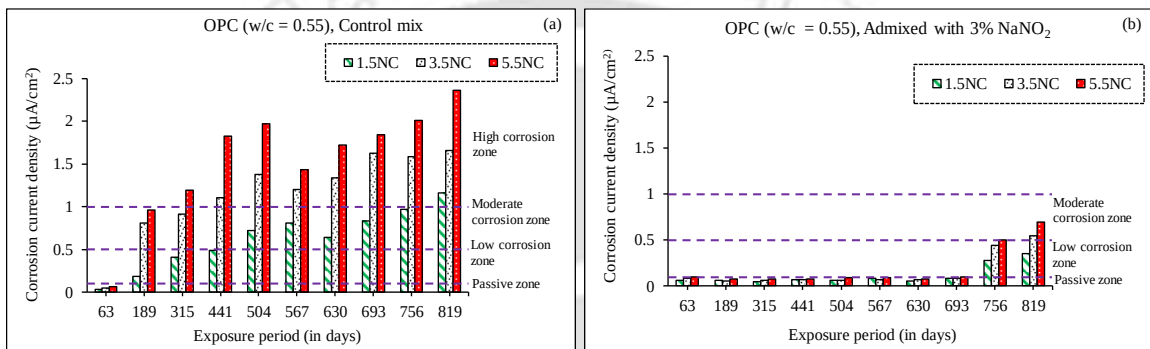


Fig. 6.15 Corrosion current density (I_{corr}) of steel reinforcement in OPC concrete at w/c of 0.55, and exposed to different concentrations of NaCl solution: (a) control mix, and (b) concrete admixed with 3% $NaNO_2$

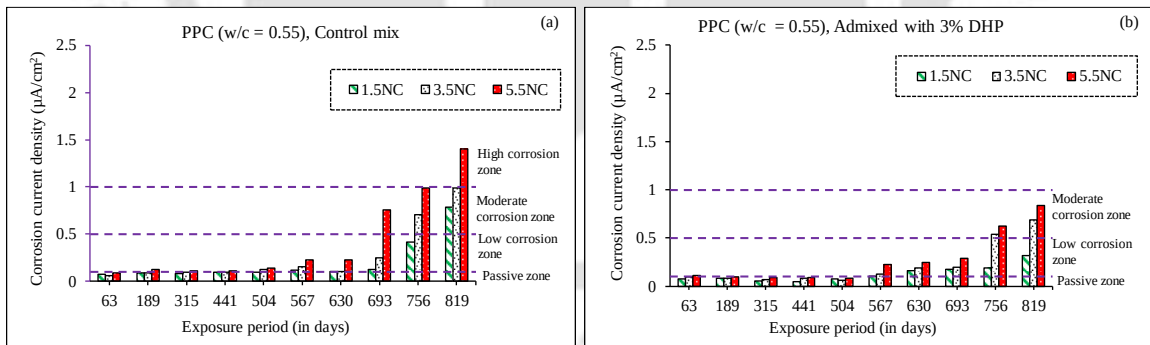


Fig. 6.16 Corrosion current density (I_{corr}) of steel reinforcement in PPC concrete at w/c of 0.55, and exposed to different concentrations of NaCl solution: (a) control mix, and (b) concrete admixed with 3% DHP

6.2.1 Effect of cation type of chloride salts and exposure solution on corrosion parameters

While comparing the effect of cation type of chloride salts on half-cell potential (E_0), and corrosion current density (I_{corr}) of steel reinforcement in concrete exposed to only chloride

solutions, the specimens exposed to 3.5% NaCl solution mostly showed more negative E_0 , and higher I_{corr} than that exposed to 3.5% CaCl_2 solution followed by 3.5% MgCl_2 solution for all the concrete mixes over the entire exposure period as observed from Fig. 6.1 to Fig. 6.4, and Fig. 6.7 to Fig. 6.10. The reason behind more negative E_0 , and higher I_{corr} in the specimens exposed to NaCl solution may be ascribed to the presence of more amount of chloride ions at rebar level as compared to CaCl_2 , and MgCl_2 solutions as evident from the measured free chloride ion (C_F) content at rebar level presented in Fig. 6.17 to Fig. 6.20 (discussed later in Section 6.3). The presence of higher free chloride ion content increases the conductivity of concrete, which increased the I_{corr} of steel reinforcement [105]. Higher amount of free chloride ion content in the concrete exposed to NaCl solution may be attributed to the decomposition of Friedel's salt due to an increase in pH of concrete in the presence of Na^+ ions that results in release of bound chloride (C_B) thereby increasing the free chloride ion (C_F) content [52]. The increase in pH of concrete pore solution in the presence of NaCl may occur due to replacement of $(\text{OH})^-$ ions present in the interlayers of AFm hydrates by chloride ions [55]. The presence of less amount of Friedel's salt (calcium chloroaluminate) in the specimens exposed to NaCl solution as compared to MgCl_2 , and CaCl_2 solutions was also observed from the XRD patterns shown in Fig. 6.23 to Fig. 6.32, and Appendix A: Fig. A13 to Fig. A22 (discussed later in Section 6.4.1). Further, the less negative E_0 , and lower I_{corr} in the specimens exposed to MgCl_2 solution may be ascribed to lower C_F content as compared to the specimens exposed to NaCl, and CaCl_2 solutions. The lower C_F content in the concrete exposed to MgCl_2 solution may be due to the effect of precipitation of brucite ($\text{Mg}(\text{OH})_2$) in the pores of the surface layers of concrete, which might have reduced further penetration of chloride ions into concrete [137]. As observed from Fig. 6.1 to Fig. 6.4, the E_0 became more negative than -350 mV (Cu/CuSO₄ electrode)/-270 mV (SCE) early in case of exposure to NaCl solution as compared to CaCl_2 solution followed by MgCl_2 solution in all concrete mixes, thereby indicating lower corrosion initiation period for the concrete exposed to NaCl solution as compared to CaCl_2 , and MgCl_2 solutions. For instance, for OPC control concrete (without corrosion inhibitor) at w/c of 0.45, the specimens exposed to 3.5% NaCl solution showed E_0 values more negative than -270 mV (SCE) at 504 days of exposure, whereas the specimens exposed to 3.5% CaCl_2 , and 3.5% MgCl_2 solutions showed E_0 values more negative than -270 mV (SCE) at exposure periods of 567 days, and 630 days, respectively. Similarly, in control concrete made from PPC at w/c of 0.45, the E_0 values became more negative than -270 mV (SCE) at the exposure period of 693 days for specimens exposed to 3.5% NaCl solution, and 756

days each for the specimens exposed to 3.5% CaCl_2 , and 3.5% MgCl_2 solutions. Further, at w/c of 0.55, the OPC control concrete specimens exposed to 3.5% NaCl solution showed E_0 values more negative than -270 mV (SCE) at 189 days of exposure, whereas the specimens exposed to 3.5% CaCl_2 , and 3.5% MgCl_2 solutions showed E_0 values more negative than -270 mV (SCE) at exposure periods of 315 days, and 441 days respectively. Similarly, in PPC control concrete at w/c of 0.55, the E_0 values became more negative than -270 mV (SCE) at the exposure period of 630 days for the specimens exposed to 3.5% NaCl solution, and 693 days each for the specimens exposed to 3.5% CaCl_2 , and 3.5% MgCl_2 solutions.

In case of concrete exposed to composite chloride-sulfate solutions, the specimens exposed to 3.5% CaCl_2 +3.5% MgSO_4 solution mostly showed more negative E_0 , and higher I_{corr} as compared to that exposed to 3.5% NaCl+3.5% MgSO_4 solution followed by 3.5% MgCl_2 +3.5% MgSO_4 solution for all concrete mixes over the entire exposure period as observed from Fig. 6.5, Fig. 6.6, Fig. 6.11, and Fig. 6.12. The more negative E_0 , and higher I_{corr} in the specimens exposed to CaCl_2 + MgSO_4 solution may be due to the presence of more amount of chloride ions at rebar level than that in the concrete exposed to NaCl+ MgSO_4 , and MgCl_2 + MgSO_4 solutions, which is substantiated with the free chloride ion (C_F) content at rebar level shown in Fig. 6.21, and Fig. 6.22. Further, less negative E_0 , and lower I_{corr} in the concrete exposed to MgCl_2 + MgSO_4 solution is ascribed to lower C_F content at rebar level as compared to that exposed to NaCl+ MgSO_4 , and CaCl_2 + MgSO_4 solutions.

From Fig 6.1, Fig. 6.5, Fig. 6.7, and Fig. 6.11, it is observed that in OPC concrete, the E_0 was mostly more negative, and I_{corr} was higher in the specimens exposed to chloride solution as compared to that exposed to composite chloride-sulfate solutions irrespective of cation type of chloride salt, and corrosion inhibitor. The reason behind this may be due to the presence of lower amount of free chloride ion content near rebar level in the concrete exposed to composite chloride-sulfate solutions as compared to that exposed to only chloride solutions, which is in line with results of free chloride ion content shown in Fig. 6.17, and Fig. 6.21. However, in PPC concrete (Fig 6.2, Fig. 6.6, Fig. 6.8, and Fig. 6.12), there was no systematic variation in E_0 , and I_{corr} of steel reinforcement in the concrete between chloride, and composite chloride-sulfate solutions.

While comparing the effect of NaCl concentration (1.5%, 3.5%, and 5.5%) in the exposure solution on variation in E_0 , and I_{corr} (Fig. 6.13 to Fig. 6.16, and Appendix A: Fig. A1 to Fig.

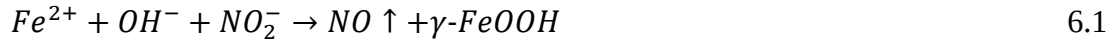
A8), it is observed that the E_0 was mostly more negative, and I_{corr} was mostly higher in the concrete exposed to higher concentration of NaCl solution than that exposed to lower concentration of NaCl solution for both cements, w/c, and corrosion inhibitors. This may be attributed to the effect of penetration of more amount of chloride ions to rebar level in the concrete exposed to NaCl solution of higher concentration as a result of higher concentration gradient of chloride ions.

6.2.2 Effect of admixed corrosion inhibitors on corrosion parameters

For both OPC, and PPC, the concrete admixed with corrosion inhibitors mostly showed less negative half-cell potential (E_0), and a significant decrease in corrosion current density (I_{corr}) as compared to control concrete (without corrosion inhibitor) irrespective of w/c, and exposure solutions (i.e., both chloride, and composite chloride-sulfate solutions) over the entire exposure period as evident from Fig. 6.1 to Fig. 6.12. Similar variations in E_0 , and I_{corr} were also observed in case of NaCl solutions of concentration 1.5%, and 5.5% (Appendix A: Fig. A1 to Fig. A8). This indicated that the addition of corrosion inhibitors enhanced the resistivity of concrete against corrosion of steel reinforcement [105]. Overall, in case of exposure to chloride solutions (i.e., 3.5% NaCl, 3.5% MgCl_2 , and 3.5% CaCl_2), the concrete mixes admixed with 1% NaNO_2 , and 1% DHP showed 8.11 times, and 7.47 times lower I_{corr} respectively as compared to the control mix at the end of the exposure period (i.e., at 819 days of exposure) irrespective of cement type, and chloride exposure solution at w/c of 0.45. Similarly, the concrete mixes admixed with 3% NaNO_2 , and 3% DHP showed 10.54 times, and 10.23 times lower I_{corr} respectively as compared to the control mix at w/c of 0.45. At w/c of 0.55, the concrete mixes admixed with NaNO_2 , and DHP showed 1.93 times, and 1.72 times lower I_{corr} respectively at 1% concentration as compared to the control mix irrespective of cement type, and chloride exposure solution. Similarly, at 3% concentration, the concrete mixes admixed with NaNO_2 , and DHP showed 5.64 times, and 3.13 times lower I_{corr} respectively as compared to the control mix at w/c of 0.55. In case of exposure to composite chloride-sulfate solutions, the concrete admixed with 3% NaNO_2 , and that admixed with 3% DHP showed 3.76 times, and 3.06 times lower I_{corr} respectively than the control mix irrespective of cement type, and exposure solution.

The corrosion inhibitors used in this investigation, i.e., sodium nitrite (SN), and di-Sodium hydrogen phosphate (DHP) protected the steel bar against corrosion in two ways. In case of sodium nitrite, the first way of protection includes nitrite-AFm formation due to reaction of NO_2^- ions with AFm (aluminato-ferrite-monosubstituent) phase of hydrated cement. The

formation of nitrite-AFm might have blocked the pores, and reduced the ingress of chloride ions into concrete admixed with NaNO_2 as compared to control concrete. In the second way of protection, NO_2^- ions compete with chloride ions to react with ferrous ions, and results in the formation of a film of stable $\gamma\text{-FeOOH}$ over the steel reinforcement, as shown in the following equation [18]:



In case of di-Sodium hydrogen phosphate (DHP), the first way of protection includes precipitation of insoluble calcium phosphate due to reaction of phosphate ions with portlandite (calcium hydroxide), which can block the concrete pores, and hinders the diffusion of oxygen, and chloride ions [104]. The second way of protection may be attributed to the formation of a protective layer of phosphate compounds such as strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) or ferric phosphate (FePO_4), which are formed as a result of reaction of phosphate ions with iron (III) ions (already discussed in Section 4.2.2, Chapter 4). Generally, the passive layer formed over the steel reinforcement embedded in concrete is composed of Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, and FeOOH [96]. However, in the presence of phosphate ions, a duplex film is likely to be formed [104]. This duplex film consists of an outer layer of ferrous phosphate formed through dissolution-precipitation mechanism (as shown in Eq. 6.2), which is progressively oxidized to ferric phosphate, and an inner protective layer of iron oxide (Fe_3O_4) formed through solid-state process [96, 104]. The outer thin layer of ferric phosphate (FePO_4), which is a poor conductor, slows down the diffusion of oxygen thereby hindering further oxidation process at the metal-film interface [96, 104, 128]. The inner iron oxide (Fe_3O_4) layer is a good conductor, and insoluble, which prevents the iron dissolution [96, 104].



As observed from Fig. 6.1 (b, c, d, e), Fig. 6.2 (b, c, d, e), Fig. 6.3 (b, c, d, e), and Fig. 6.4 (b, c, d, e), the half-cell potential of steel reinforcement was mostly more negative in the concrete admixed with NaNO_2 as compared to that admixed with DHP during the initial exposure period (i.e., till about 504 days for w/c of 0.45, and about 315 days for w/c of 0.55), whereas during the later exposure period (i.e., after 504 days for w/c of 0.45, and after 315 days for w/c of 0.55), the opposite variation was observed for both cements, and all chloride exposure solutions. In addition, the half-cell potential of steel reinforcement became more negative than -270 mV (SCE) after a comparatively longer exposure period

for NaNO_2 as compared to DHP for both cements, and all chloride exposure solutions. At w/c of 0.45, the I_{corr} of steel reinforcement was mostly higher in the concrete admixed with NaNO_2 as compared to that admixed with DHP during the early exposure period (i.e., till about 504 days), whereas after that (i.e., after 504 days), the opposite variation was observed for both cements, and all chloride solutions. In case of concrete mixes prepared at w/c of 0.55, the specimens admixed with NaNO_2 mostly showed lower I_{corr} as compared to those admixed with DHP over the entire exposure period for both cements, and all chloride solutions except in few cases during the early exposure period (i.e., till about 315 days) where the opposite variation was observed. The more negative E_0 , and higher I_{corr} in the concrete admixed with NaNO_2 during the early exposure period may be attributed to the dominant effect of alteration in oxygen, and moisture content near rebar level over the effect of chloride ions as there may be presence of lower chloride content near rebar level due to ingress of less amount of chloride ions during the early exposure period. Further, the difference in I_{corr} between NaNO_2 , and DHP became more substantial during the later exposure period, i.e., the specimens admixed with DHP exhibited significantly higher I_{corr} as compared to those admixed with NaNO_2 . This indicates that the specimens admixed with NaNO_2 offered improved resistance against chloride induced corrosion of steel reinforcement as compared to DHP even in the presence of higher amount of chloride ions near steel reinforcement as a result of penetration of more amount of chloride ions into concrete during the later exposure period. The higher I_{corr} of steel reinforcement in the concrete admixed with DHP as compared to NaNO_2 may be attributed to the effect of formation of calcium phosphate (due to reaction of phosphate ions with calcium hydroxide), which decreases the availability of phosphate ions thereby affecting the formation of protective film over the steel surface to a certain degree. The lower I_{corr} of steel reinforcement in the concrete admixed with NaNO_2 may be ascribed to the formation of a stable protective layer of iron oxide over the steel surface as a result of preferential reaction of NO_2^- ions over chloride ions with the ferrous ions.

With increase in admixed dosage of both corrosion inhibitors from 1% to 3%, the E_0 became mostly less negative as well as the I_{corr} mostly decreased in case of concrete exposed chloride solutions (3.5% NaCl , 3.5% MgCl_2 , and 3.5% CaCl_2) thereby indicating greater efficiency of the corrosion inhibitors at higher dosage in reducing the chloride induced corrosion of steel reinforcement in concrete. Similar variations in E_0 , and I_{corr} were also observed with increase in admixed dosage of corrosion inhibitors in case of exposure

to NaCl solutions of concentration 1.5%, and 5.5%. From Fig. 6.1 (b, c, d, e), Fig. 6.2 (b, c, d, e), Fig. 6.3 (b, c, d, e), and Fig. 6.4 (b, c, d, e), it is noted that the E_0 reached the threshold value of -270 mV (SCE) in a shorter exposure period at lower dosage (1%) of the inhibitor as compared to higher dosage (3%) for both cements, w/c, corrosion inhibitors, and all chloride exposure solutions. Similar variation in I_{corr} was observed between lower, and higher dosages of corrosion inhibitors with respect to different zones of corrosion during the later exposure period where the I_{corr} at 1% dosage lie in the zones corresponding to higher level of corrosion as compared to 3% dosage. The improved performance of corrosion inhibitors at higher dosage may be attributed to the availability of higher concentration of nitrite, and phosphate ions in concrete, which resulted in reduced ingress of chloride ions due to blocking of concrete pores as a result of reaction of nitrite, and phosphate ions individually with the hydrated cement phases as well as formation of protective layer over the steel surface to a greater degree at higher concentration of nitrite, and phosphate ions. Further, the addition of higher dosage of NaNO_2 , and DHP in the concrete might have maintained the $[\text{NO}_2^-]/[\text{Cl}^-]$ ratio, and $[\text{PO}_4^{3-}]/[\text{Cl}^-]$ ratio, which is required to inhibit the corrosion of steel reinforcement [82]. In few cases, the lower extent of corrosion at lower dosage of corrosion inhibitors may be ascribed to the effect of alterations in the reaction of the corrosion inhibitors with the hydrated cement phases in concrete. Overall, at the end of exposure period (i.e., at 819 days of exposure), the I_{corr} of steel reinforcement in the concrete containing NaNO_2 was 1.39 times lower as compared to that in the concrete containing DHP irrespective of cement type, w/c, dosage of corrosion inhibitor, and chloride exposure solution.

In case of concrete exposed to composite chloride-sulfate solutions, there was no systematic variation in half-cell potential (E_0), and corrosion current density (I_{corr}) of steel reinforcement between NaNO_2 , and DHP for both cements, and all composite chloride-sulfate solutions. Further, the E_0 values were less negative than -270 mV (SCE), and the I_{corr} values were mostly in the passive zone (I_{corr} : less than $0.1 \mu\text{A}/\text{cm}^2$) over the entire exposure period for both corrosion inhibitors as evident from Fig. 6.5 (b, c), Fig. 6.6 (b, c), Fig. 6.11 (b, c), and Fig. 6.12 (b, c). These variations in E_0 , and I_{corr} of steel reinforcement between NaNO_2 , and DHP may be attributed to the effect of lower free chloride ion content near rebar level in the concrete exposed to composite chloride-sulfate solutions due to penetration of comparatively lower amount of chloride ions into the concrete.

6.2.3 Effect of cement type and w/c on corrosion parameters

From Fig. 6.1 to Fig. 6.4, and Fig. 6.7 to Fig. 6.10, it is observed that the E_0 was mostly more negative as well as the I_{corr} was mostly higher in the concrete prepared with PPC as compared to that prepared with OPC during the initial exposure period (i.e., till about 504 days for w/c of 0.45, and about 315 days for w/c of 0.55), whereas the opposite variation was observed during the later exposure period (i.e., after 504 days, and 315 days for w/c of 0.45, and 0.55 respectively) for both corrosion inhibitors and all chloride exposure solutions. Similar variations in E_0 , and I_{corr} between OPC, and PPC were also observed in the concrete exposed to composite chloride-sulfate solutions (Fig. 6.5, Fig. 6.6, Fig. 6.11, and Fig. 6.12), and those exposed to 1.5%, and 5.5% NaCl solutions (Appendix A: Fig. A1 to Fig. A8). It may be noted that, during the early exposure period, there may be presence of lower amount of chloride ions near the rebar level due to ingress of less amount of chloride ions. Thus, more negative E_0 , and higher I_{corr} in the concrete made with PPC during the early exposure period may be due to the significant effect of alteration in the oxygen, and moisture content near the steel reinforcement level over the effect of chloride ions. The less negative E_0 , and lower I_{corr} of steel reinforcement in the concrete made with PPC as compared to OPC during the later exposure period may be ascribed to the effect of formation of denser microstructure in PPC concrete as a result of production of more amount of C-S-H due to pozzolanic reaction, which reduced the penetration of chloride ions into PPC concrete as compared to OPC concrete. This is line with the free chloride ion (C_F) content near rebar level (i.e., in depth interval of 25-30 mm from exposure surface) where the C_F content near rebar level was lower in PPC concrete than OPC concrete for both corrosion inhibitors, and all exposure solutions as evident from Fig. 6.17 to Fig. 6.22, and Appendix A: Fig. A9 to Fig. A12. As observed from Fig. 6.7 to Fig. 6.12, and Appendix A: Fig. A5 to Fig. A8, in PPC concrete, the I_{corr} of steel reinforcement was mostly in the passive zone for a substantial period of exposure whereas in OPC concrete, the I_{corr} was mostly in passive zone for a shorter exposure period irrespective of w/c, corrosion inhibitor, and exposure solution (i.e., chloride, and composite chloride-sulfate solutions). For instance, in PPC concrete at w/c of 0.55, the I_{corr} of steel reinforcement was mostly in the passive zone till about 693 days of exposure followed by reaching low to moderate corrosion zones only towards the end of exposure period irrespective of the addition of corrosion inhibitors in concrete as observed from Fig. 6.10. However, in OPC concrete at w/c of 0.55, the I_{corr} was mostly in the passive zone for a shorter exposure period, i.e., till

about 315 days of exposure followed by: i) reaching low to high corrosion zones thereafter in case of control mix, and the concrete mix admixed with 1% corrosion inhibitor (both NaNO_2 , and DHP), and ii) reaching low to moderate corrosion zones, thereafter in case of the concrete mix admixed with 3% DHP, and towards end of exposure period in case of the concrete mix admixed with 3% NaNO_2 as evident from Fig. 6.9. This indicated that the corrosion inhibitors were comparatively more effective in reducing the extent of corrosion of steel reinforcement in OPC concrete as compared to PPC concrete. In PPC concrete, the formation of denser microstructure had dominant effect on minimizing the extent of corrosion over the effect of corrosion inhibitors as the formation of denser microstructure reduced the penetration of chloride ions thereby resulting in significantly lower I_{corr} in PPC concrete than OPC concrete. Overall, at the end of exposure period, the I_{corr} in PPC concrete was 2.41 times lower as compared to OPC concrete irrespective of w/c, corrosion inhibitor, and chloride exposure solution. Similarly, in case of exposure to composite chloride-sulfate solutions, the I_{corr} in PPC concrete was 1.83 times lower than OPC concrete at the end of exposure period irrespective of corrosion inhibitor, and exposure solution.

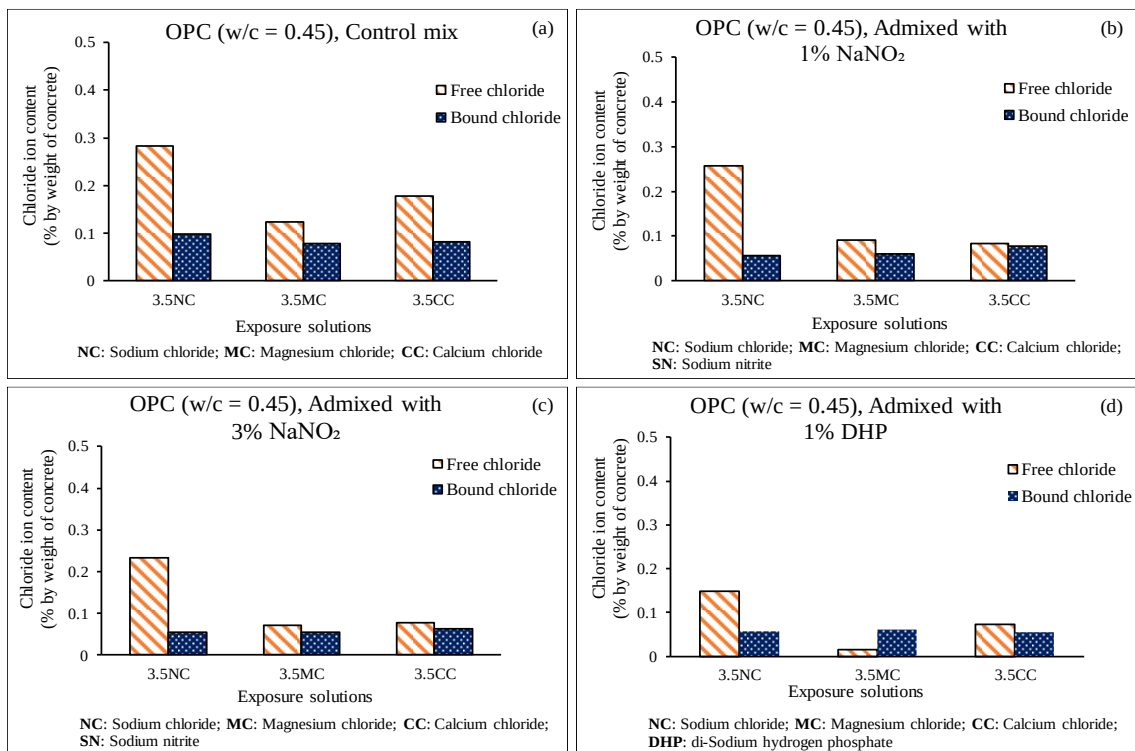
While comparing the effect of w/c, i.e., 0.45, and 0.55 on half-cell potential (E_0) (Fig. 6.1 to Fig. 6.4, Appendix A: Fig. A1 to Fig. A4), and corrosion current density (I_{corr}) (Fig. 6.7 to Fig. 6.10, Appendix A: Fig. A5 to Fig. A8) of steel reinforcement, it is observed that the E_0 values became mostly more negative, and the I_{corr} values increased with increase in w/c over the entire exposure period for both cements, corrosion inhibitors, and all chloride exposure solutions. This may be attributed to the effect of presence of higher amount of free chloride near rebar level in the concrete made with higher w/c due to penetration of more amount of chloride ions into concrete as compared to that made with lower w/c. The presence of higher free chloride ion content in the concrete made with w/c of 0.55 than that made with 0.45 is observed from the results shown in Fig. 6.17 to Fig. 6.20, and Appendix A: Fig. A9 to Fig. A12.

From Fig. 6.1 to Fig. 6.12, and Appendix A: Fig. A1 to Fig. A8, it is observed that the variation in E_0 , and I_{corr} of steel reinforcement with exposure period was not systematic till the I_{corr} was in passive zone, i.e., below the approximate limit for passivity of steel reinforcement. However, when I_{corr} entered the low corrosion zone thereby indicating initiation of corrosion, the E_0 values became mostly more negative, and the I_{corr} values increased with increase in exposure period for all exposure solutions, cements, w/c, and

corrosion inhibitors. This may be attributed to the effect of ingress of more amount of chloride ions into the concrete with increase in exposure period.

6.3 Chloride ion content

The free chloride ion (C_F), and bound chloride ion (C_B) contents of concrete powder samples collected from near the rebar level (i.e., depth interval of 25-30 mm from exposure surface) of cylindrical reinforced concrete specimens made with w/c of 0.45, and 0.55; admixed with, and without corrosion inhibitors; and exposed to different chloride salt solutions are shown in Fig. 6.17, and Fig. 6.19 for OPC, and Fig. 6.18, and Fig. 6.20 for PPC. Similarly, the free chloride ion (C_F), and bound chloride ion (C_B) contents of concrete mixes exposed to composite chloride-sulfate solutions are shown in Fig. 6.21 for OPC, and Fig. 6.22 for PPC. Further, the C_F and C_B contents of concrete mixes exposed to 1.5%, and 5.5% NaCl solutions are shown in Appendix A: Fig. A9 to Fig. A12. The results of chloride content shown in these figures correspond to the exposure period when the half-cell potential became more negative than -270 mV (SCE). In case of concrete mixes where the half-cell potential values were less negative than -270 mV (SCE) till the end of exposure period, the chloride content of those concrete mixes were determined at the end of exposure period, i.e., 819 days.



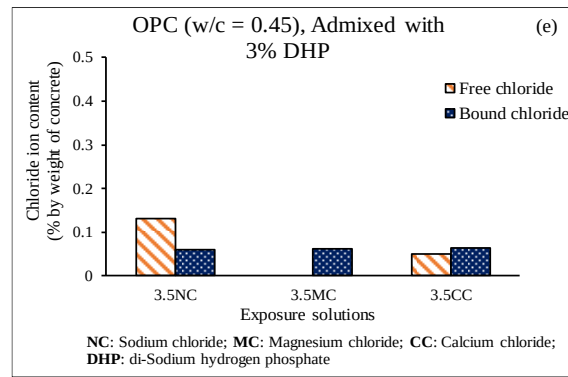


Fig. 6.17 Free, and bound chloride ion contents of OPC concrete at w/c of 0.45, and exposed to 3.5% chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂): (a) control mix, (b) concrete admixed with 1% NaNO₂, (c) concrete admixed with 3% NaNO₂, (d) concrete admixed with 1% DHP, and (e) concrete admixed with 3% DHP

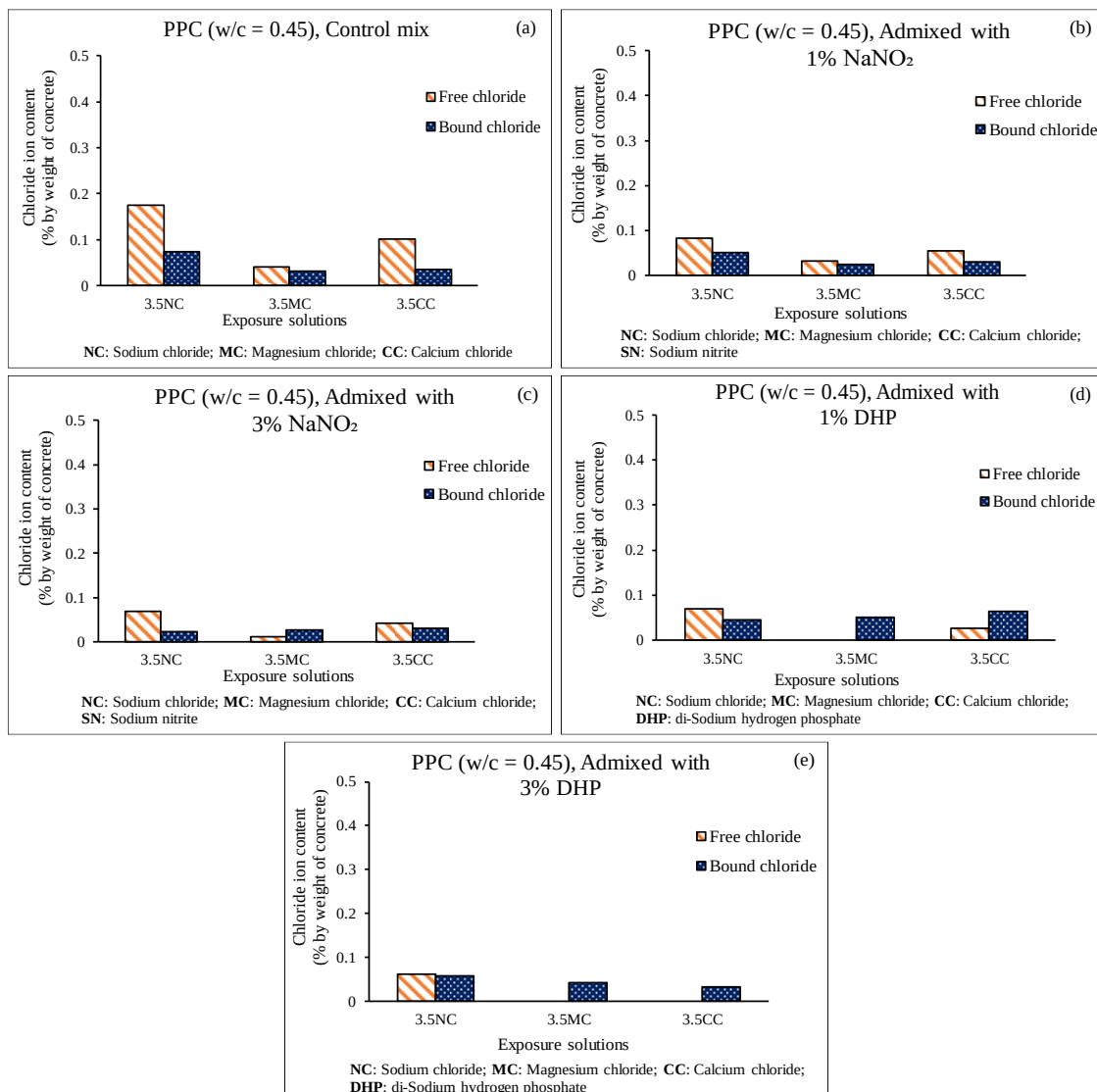


Fig. 6.18 Free, and bound chloride ion contents of PPC concrete at w/c of 0.45, and exposed to 3.5% chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂): (a) control mix, (b) concrete admixed with 1% NaNO₂, (c) concrete admixed with 3% NaNO₂, (d) concrete admixed with 1% DHP, and (e) concrete admixed with 3% DHP

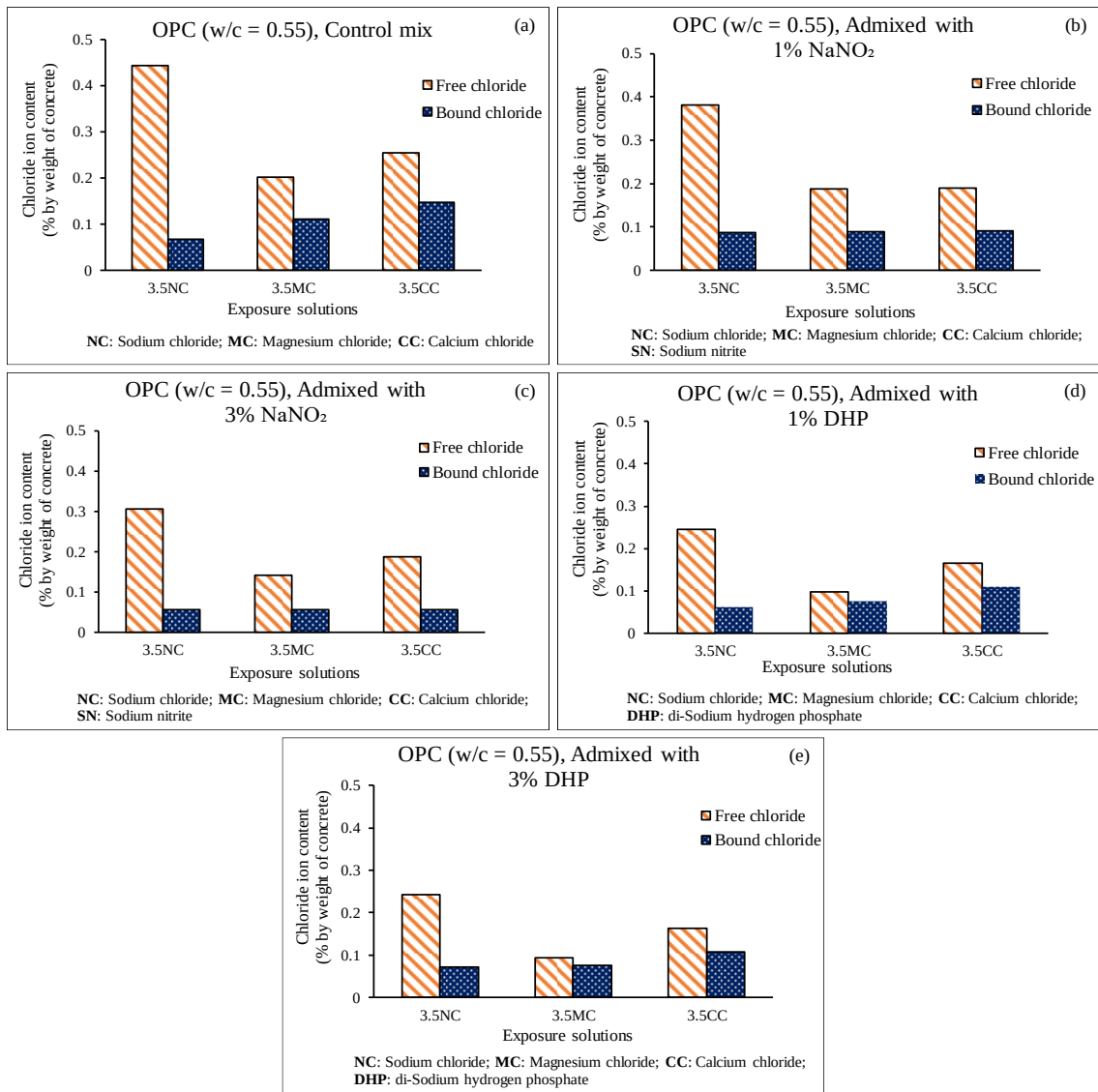
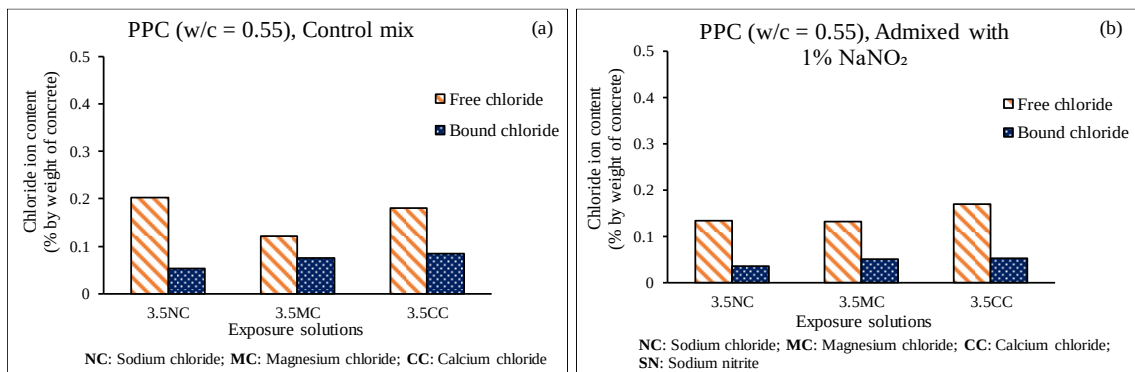


Fig. 6.19 Free, and bound chloride ion contents of OPC concrete at w/c of 0.55, and exposed to 3.5% chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂): (a) control mix, (b) concrete admixed with 1% NaNO₂, (c) concrete admixed with 3% NaNO₂, (d) concrete admixed with 1% DHP, and (e) concrete admixed with 3% DHP



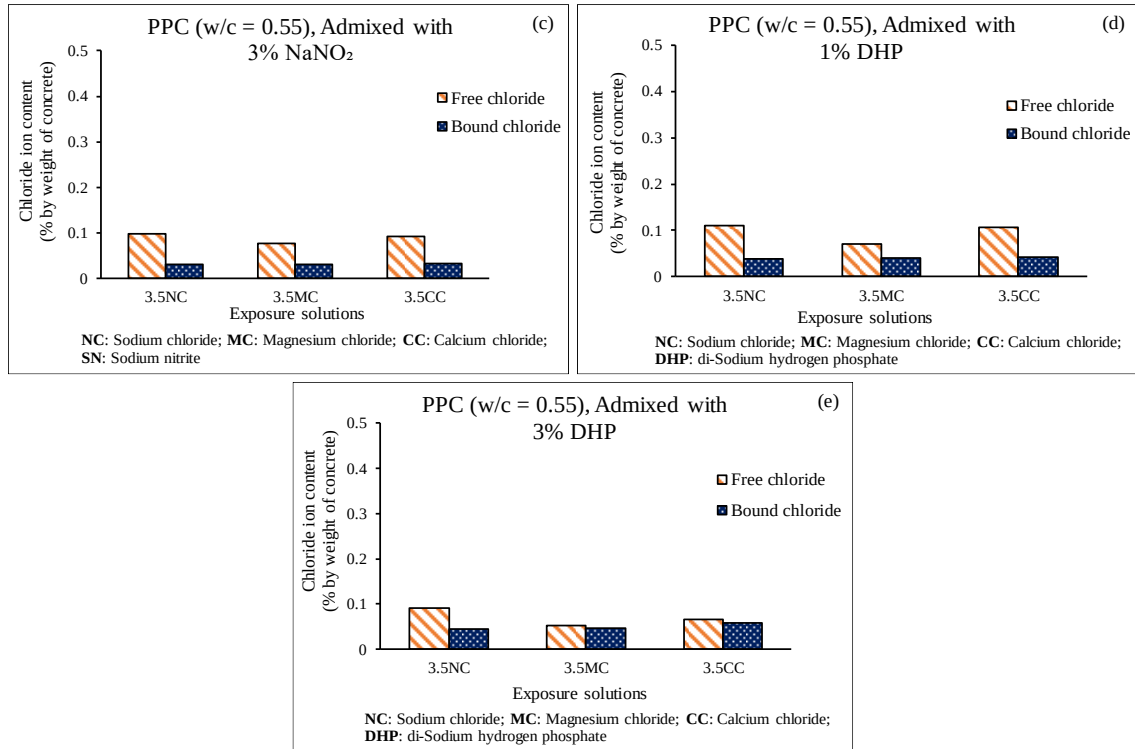


Fig. 6.20 Free, and bound chloride ion contents of PPC concrete at w/c of 0.55, and exposed to 3.5% chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂): (a) control mix, (b) concrete admixed with 1% NaNO₂, (c) concrete admixed with 3% NaNO₂, (d) concrete admixed with 1% DHP, and (e) concrete admixed with 3% DHP

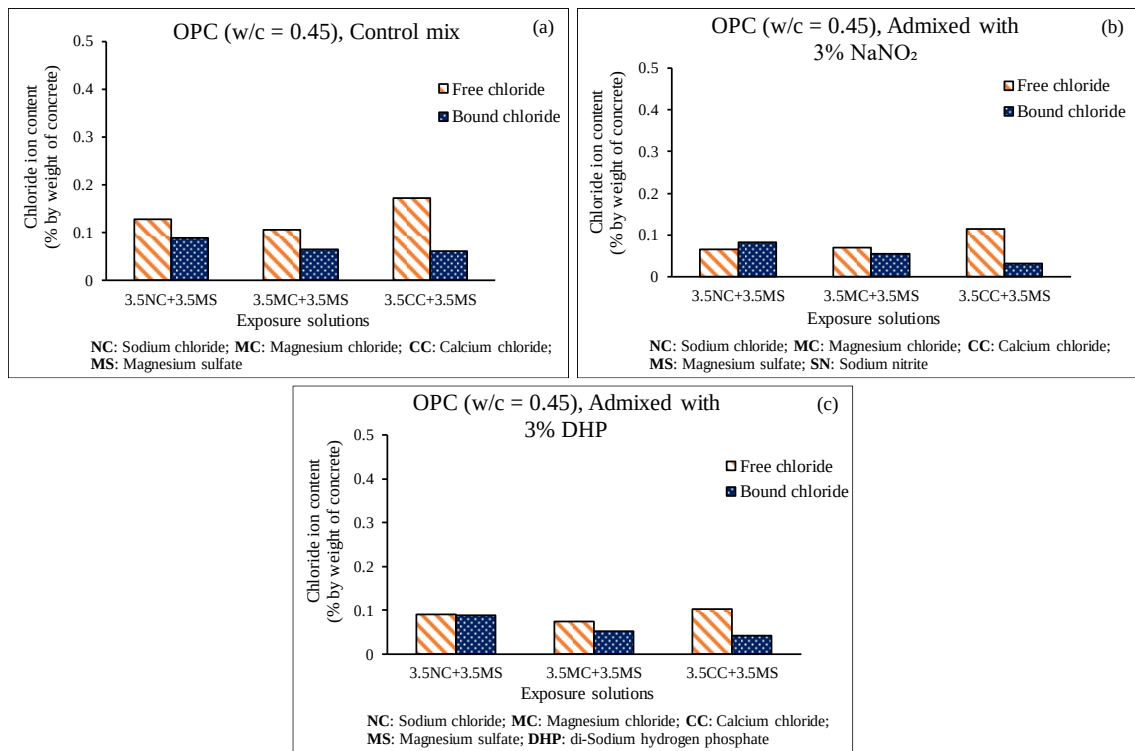


Fig. 6.21 Free, and bound chloride ion contents of OPC concrete at w/c 0.45, and exposed to composite chloride-sulfate solutions: (a) control mix, (b) concrete admixed with 3% NaNO₂, and (c) concrete admixed with 3% DHP

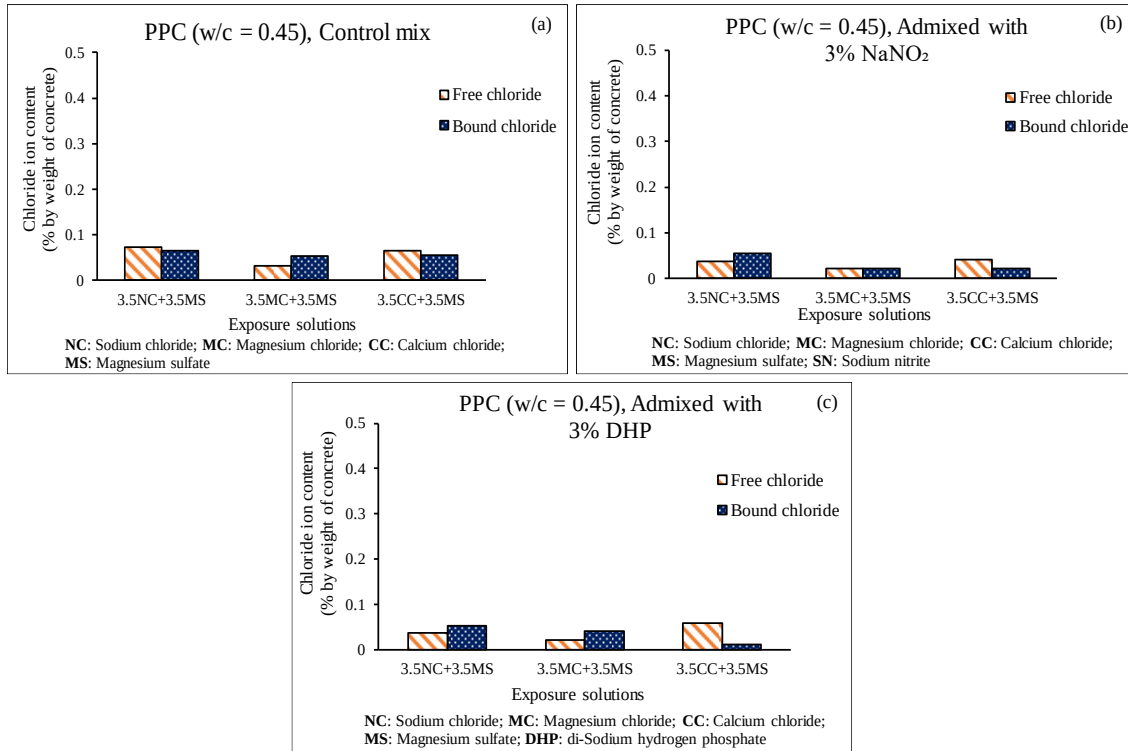


Fig. 6.22 Free, and bound chloride ion contents of PPC concrete at w/c 0.45, and exposed to composite chloride-sulfate solutions: (a) control mix, (b) concrete admixed with 3% NaNO₂, and (c) concrete admixed with 3% DHP

From Fig. 6.17 to Fig. 6.22, and Appendix A: Fig. A9 to Fig. A12, it is observed that PPC concrete showed lower free chloride ion (C_F) content as compared to OPC concrete in case of control specimens (without corrosion inhibitors) as well as those admixed with corrosion inhibitors for all chloride, and composite chloride-sulfate exposure solutions at both w/c. The lower C_F content in PPC concrete is attributed to the effect of ingress of lower amount of chloride ions as compared to OPC concrete. As stated earlier, the formation of denser microstructure in PPC concrete as a result of formation of additional C-S-H from the pozzolanic reaction reduced the penetration of chloride ions into concrete. While comparing the bound chloride ion (C_B) content between OPC, and PPC, it is noted that OPC concrete showed higher chloride binding as compared to PPC concrete irrespective of w/c, presence of corrosion inhibitors, and type of chloride salt in the chloride, and composite chloride-sulfate exposure solutions. This may be attributed to the effect of formation of higher amount of Friedel's salt in OPC concrete (evident from the weight (%) of compounds estimated from XRD analysis as shown in Fig. 6.39 to Fig. 6.44) due to reaction of chloride ions with C_3A to a greater extent. Both higher C_F , and C_B contents in OPC concrete mixes are due to the penetration of more amount of chloride ions into the concrete. Further, the free chloride, and bound chloride ion contents were higher in the

concrete mixes made with w/c of 0.55 as compared to that made with w/c of 0.45 irrespective of cement type, presence of corrosion inhibitors, and chloride exposure solutions as evident from Fig. 6.17 to Fig. 6.20, and Appendix A: Fig. A9 to Fig. A12. This may be ascribed to the effect of penetration of higher amount of chloride ions into the concrete mixes made with higher w/c, i.e., 0.55 as compare to w/c of 0.45.

From Fig. 6.17 to Fig. 6.20, it is noted that, in case of chloride (i.e., NaCl, MgCl₂, and CaCl₂) solutions, the specimens exposed to NaCl solution showed higher C_F content than that exposed to CaCl₂ solution followed by MgCl₂ solution for both cements, w/c, and irrespective of presence of corrosion inhibitors. The higher C_F content in the specimens exposed to NaCl solution may be attributed to the increase in alkalinity of concrete pore solution in the presence of Na⁺ ions that resulted in release of chloride ions from Friedel's salt [135]. Further, NaCl diffuses into concrete at a higher rate as compared to MgCl₂, and CaCl₂, which results in availability of more amount of chloride ions near rebar level in the cylindrical specimens exposed to NaCl solution [187]. The lower C_F content in the concrete exposed to MgCl₂ solution may be ascribed to the effect of much slower diffusion rate of MgCl₂ into the concrete as compared to NaCl, and CaCl₂ [37, 187]. In addition, the formation of brucite (magnesium hydroxide) in the concrete exposed to MgCl₂ solution might have filled the pores, which hindered the ingress of chloride ions into the concrete. The formation of brucite in the concrete exposed to MgCl₂ solution is evident from the XRD patterns shown in Fig. 6.23 to Fig. 6.32, and Appendix A: Fig. A13 to Fig. A22.

From Fig. 6.17 to Fig. 6.20 (for chloride exposure solutions), it is observed that the bound chloride ion (C_B) content was higher in the concrete exposed to CaCl₂ solution than MgCl₂ solution followed by NaCl solution for OPC as well as for PPC irrespective of w/c, and presence of corrosion inhibitors. The higher extent of chloride binding in the concrete exposed to CaCl₂ solution may be due to the dominant effect of formation of more amount of Friedel's salt as compared to MgCl₂, and NaCl solutions. The formation of more amount of Friedel's salt in the concrete exposed to CaCl₂ solution than MgCl₂ solution followed by NaCl solution is substantiated by the weight (%) of Friedel's salt estimated from the XRD analysis as shown in Fig. 6.39 to Fig. 6.42. Although there is formation of comparatively more amount of calcium hypochlorite in the concrete exposed to MgCl₂ solution as compared to CaCl₂ solution (observed from the results of XRD analysis, Fig. 6.23 to Fig. 32, and Appendix A: Fig. A13 to Fig. A22), the formation of lower amount of Friedel's salt as well as lower extent of physical binding of chloride ions with C-S-H due to conversion

of C-S-H into M-S-H in the presence of Mg^{2+} ions resulted in lower bound chloride ion content in case of exposure to $MgCl_2$ solution as compared to $CaCl_2$ solution. As stated earlier, the higher alkalinity of concrete pore solution in the presence of Na^+ ions in the concrete subjected to $NaCl$ solution resulted in decomposition of Friedel's salt thereby releasing chloride ions, and exhibiting lower C_B content in the concrete exposed to $NaCl$ solution.

In case of exposure to composite chloride-sulfate solutions, the free chloride ion (C_F) content was mostly higher in the concrete exposed to $CaCl_2+MgSO_4$ solution as compared to $NaCl+MgSO_4$ solution followed by $MgCl_2+MgSO_4$ solution irrespective of cement type, and presence of corrosion inhibitor as evident from Fig. 6.21, and Fig. 6.22. The higher C_F content in the concrete exposed to $CaCl_2+MgSO_4$ solution may be ascribed to the decomposition of Friedel's salt in the presence of sulfate ions to a greater extent, which resulted in release of bound chloride to a higher extent. The lower C_F content in the concrete exposed to $MgCl_2+MgSO_4$ solution as compared to $NaCl+MgSO_4$ solution may be attributed to the effect of penetration of lower amount of chloride ions into the concrete in case of exposure to $MgCl_2+MgSO_4$ solution.

In case of composite chloride-sulfate solutions, the bound chloride ion content was higher in the concrete exposed to $NaCl+MgSO_4$ solution as compared to $MgCl_2+MgSO_4$ solution followed by $CaCl_2+MgSO_4$ solution. This is attributed to the effect of formation of comparatively higher amount of calcium chloroaluminate (Friedel's salt) in case of exposure to $NaCl+MgSO_4$ solution than $MgCl_2+MgSO_4$ solution followed by $CaCl_2+MgSO_4$ solution. The formation of higher amount of Friedel's salt in the concrete exposed to $NaCl+MgSO_4$ solution is evident from the weight (%) of Friedel's salt estimated from XRD analysis (Fig. 6.43, and Fig. 6.44). The higher bound chloride ion content in the concrete exposed to $MgCl_2+MgSO_4$ solution as compared to $CaCl_2+MgSO_4$ solution may be attributed to the formation of more quantity of calcium chloroaluminate, and calcium hypochlorite in the concrete exposed to $MgCl_2+MgSO_4$ solution as compared to $CaCl_2+MgSO_4$ solution. The formation of more amount of calcium chloroaluminate, and calcium hypochlorite in the concrete exposed to $MgCl_2+MgSO_4$ than that exposed to $CaCl_2+MgSO_4$ is evident from the XRD analysis (Fig. 6.33 to Fig. 6.38). As stated earlier, the decomposition of calcium chloroaluminate in the presence of sulfate ions might have taken place to a greater extent in the concrete exposed to $CaCl_2+MgSO_4$ solution as

compared to other composite chloride-sulfate solutions, which resulted in higher C_F content, and lower C_B content in the concrete exposed to $\text{CaCl}_2 + \text{MgSO}_4$ solution.

From Fig. 6.17, Fig. 6.18, Fig. 6.21, and Fig. 6.22, it is observed that the C_F content, and C_B content were higher in the concrete exposed to chloride solutions as compared to composite chloride-sulfate solutions irrespective of chloride salt in the exposure solution, cement type, and presence of corrosion inhibitors. The reason behind lower C_F content near rebar level in the concrete subjected to composite chloride-sulfate solutions may be ascribed to the presence of sulfate ions that hindered the ingress of chloride ions, and resulted in blocking of pores in the concrete with ettringite, and gypsum, which are formed in the presence of sulfate ions. The reaction of sulfate ions with C_3A results in the formation of ettringite in concrete. Further, calcium chloroaluminate (formed due to reaction of chloride ions with C_3A) is converted to ettringite in the presence of sulfate ions [188]. In case of exposure of concrete to composite chloride-sulfate solutions, the preferential reaction of sulfate ions over chloride ions with C_3A resulted in formation of more amount of ettringite, and lower amount of calcium chloroaluminate when compared with exposure to only chloride solutions, which is confirmed from the results of XRD analysis shown in Fig. 6.23, Fig. 6.25, Fig. 6.32 to Fig. 6.38, and Appendix A: Fig. A17, Fig. A18, and Fig. A20 for both cements, and corrosion inhibitors. In addition, the formation of brucite (magnesium hydroxide) in the presence of MgSO_4 might have also blocked the pores, and reduced the ingress of chloride ions into the concrete exposed to composite chloride-sulfate solutions.

Fig. 6.17 to Fig. 6.22, and Appendix A: Fig. A9 to Fig. A12, it is observed that the addition of corrosion inhibitors in concrete decreased the free chloride ion (C_F) content near rebar level than control concrete (without corrosion inhibitors) irrespective of cement type, w/c, and exposure solution (chloride as well as composite chloride-sulfate solutions). The reason behind this may be the formation of different compounds such as nitrite-AFm in case of addition of NaNO_2 , and calcium phosphate in case of addition of DHP (as stated earlier) that might have blocked the pores, and reduced the ingress of chloride ions into concrete. Further, the bound chloride ion (C_B) content was mostly higher in case of control concrete as compared to that containing corrosion inhibitors for both cements, w/c, and all exposure solutions. However, the extent of chemical binding of chloride ions was more in the concrete containing corrosion inhibitors (i.e., NaNO_2 , and DHP) as compared to control mix as indicated by the weight (%) of Friedel's salt estimated from the XRD analysis (Fig.

6.39 to Fig. 6.44). Thus, higher C_B content in control concrete may be due to the significant effect of higher extent of physical binding of chloride ions with C-S-H as compared to the concrete containing corrosion inhibitors. Subsequently, both higher free chloride, and bound chloride contents in control concrete is attributed to the penetration of more amount of chloride ions as compared to those containing corrosion inhibitors.

Between NaNO_2 , and DHP, the free chloride ion content was higher in the concrete admixed with NaNO_2 as compared to DHP irrespective of cement type, w/c, and type of chloride solution as evident from Fig. 6.17 (b, c, d, e), Fig. 6.18 (b, c, d, e), Fig. 6.19 (b, c, d, e), Fig. 6.20 (b, c, d, e), and Appendix A: Fig. A9 to Fig. A12. It may be noted that the corrosion current density (I_{corr}) of steel reinforcement was lower in the concrete admixed with NaNO_2 . As stated earlier, this may be attributed to the formation of a stable protective layer of iron oxide over the surface of steel reinforcement due to preferential reaction of NO_2^- ions over chloride ions with the ferrous ions. Further, the bound chloride ion content was mostly higher in the concrete admixed with DHP than that admixed with NaNO_2 . The higher extent of chloride binding in the concrete admixed with DHP as compared to NaNO_2 may be due to the dominant effect of formation of chlorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{Cl}$) [189] as well as higher extent of physical binding of chloride ions in the concrete containing DHP than that containing NaNO_2 . The higher extent of chloride binding in the concrete admixed with DHP reduced the free chloride ion content as compared to that admixed with NaNO_2 . While comparing the effect of dosage of corrosion inhibitor, it is observed from Fig. 6.17 (b, c, d, e), Fig. 6.18 (b, c, d, e), Fig. 6.19 (b, c, d, e), Fig. 6.20 (b, c, d, e), and Appendix A: Fig. A9 to Fig. A12 that the free chloride ion content decreased with increase in dosage of corrosion inhibitors (i.e., NaNO_2 , and DHP) from 1% to 3% for both cements, w/c, and all chloride exposure solutions. The lower free chloride ion content at higher dosage of corrosion inhibitors is ascribed to the effect formation of inhibitor based compounds (as stated earlier) to a higher extent thereby filling the pores, and reducing the ingress of chloride ions into the concrete to a greater extent as compared to that at lower dosage of corrosion inhibitors. Further, the bound chloride ion content in concrete increased with increase in dosage of DHP whereas in case of NaNO_2 , the bound chloride ion content decreased with increase in its dosage, for both cements, w/c, and all chloride solutions as observed from Fig. 6.17 (b, c, d, e), Fig. 6.18 (b, c, d, e), Fig. 6.19 (b, c, d, e), Fig. 6.20 (b, c, d, e), and Appendix A: Fig. A9 to Fig. A12. The higher bound chloride ion content in the concrete at higher dosage of DHP may be due to the dominant effect of formation of more

amount of chlorapatite over the effect of formation of lower amount of Friedel's salt at higher dosage as compared to that at lower dosage, which is in line with the obtained results of XRD analysis (discussed in next section). The higher C_B content in the concrete at lower dosage of NaNO_2 may be ascribed to the significant effect of physical binding of chloride ions with C-S-H over the effect of formation of lower amount of Friedel's salt at lower dosage as compared to that at higher dosage. The formation of lower amount of Friedel's salt in the concrete at lower dosage of NaNO_2 than that at higher dosage is indicated by the results of XRD analysis (discussed subsequently in next section). In case of exposure to composite chloride-sulfate solutions, there was no systematic variation in free chloride, and bound chloride ion contents near rebar level in the concrete between the corrosion inhibitors (i.e., DHP, and NaNO_2) irrespective of cement type, and chloride salt in the exposure solutions as observed from Fig. 6.21 (b, c), and Fig. 6.22 (b, c).

6.4 Microstructure study

6.4.1 X-ray diffraction (XRD) analysis

Fig. 6.23 to Fig. 6.38 show the typical XRD patterns of concrete mixes prepared from OPC, and PPC (admixed with, and without corrosion inhibitors, and exposed to chloride, and composite chloride-sulfate solutions), where portlandite (calcium hydroxide, CH), calcium chloroaluminate (CCA), ettringite (E), quartz (Q), feldspar (F), and calcium carbonate (CCB) were identified in all the XRD patterns. The remaining XRD patterns of concrete mixes prepared from OPC, and PPC are presented in Appendix A: Fig. A13 to Fig. A22. The above XRD patterns were obtained from the concrete powder samples collected from near the rebar level of cylindrical reinforced concrete specimens.

As stated earlier in Chapter 3, from the obtained XRD patterns, the weight (%) of compounds, namely ettringite (E), calcium chloroaluminate (Friedel's salt, CCA), portlandite (calcium hydroxide, CH), calcium carbonate (calcite, CCB), and quartz (Q) were estimated from semi-quantification analysis using reference intensity ratio (RIR) matrix-flushing method. The plots of weight (%) of different compounds of concrete obtained from semi-quantification analysis are shown in Fig. 6.39 to Fig. 6.42 for concrete exposed to chloride solutions, and in Fig. 6.43, and Fig. 6.44 for concrete exposed to composite chloride-sulfate solutions.

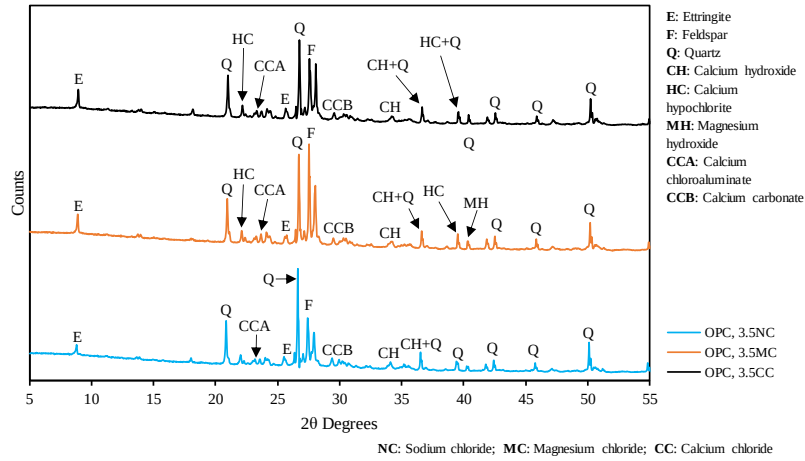


Fig. 6.23 XRD patterns of control concrete made from OPC at w/c of 0.45, and exposed to different chloride salt solutions

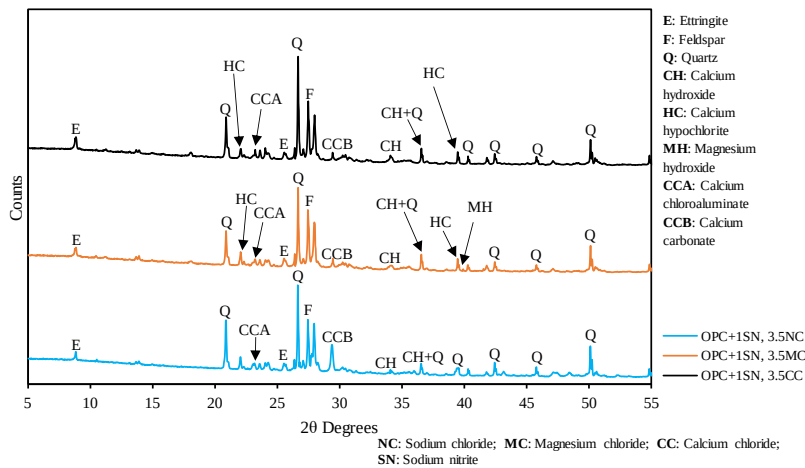


Fig. 6.24 XRD patterns of OPC concrete admixed with 1% NaNO_2 at w/c of 0.55, and exposed to different chloride salt solutions

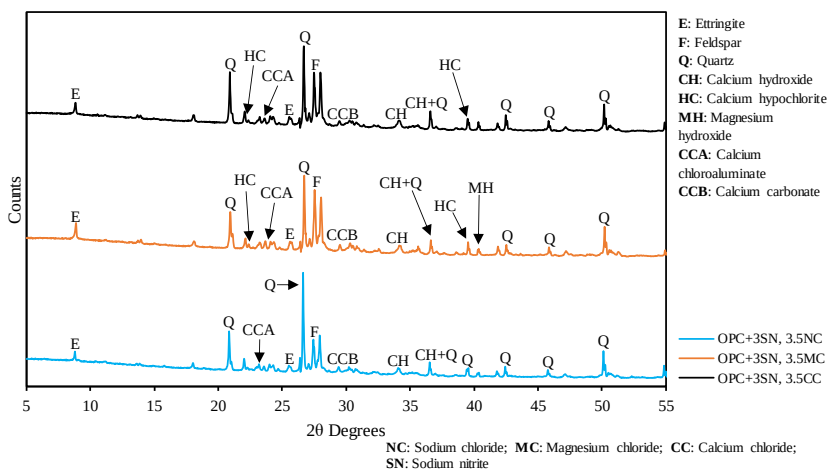


Fig. 6.25 XRD patterns of OPC concrete admixed with 3% NaNO_2 at w/c of 0.45, and exposed to different chloride salt solutions

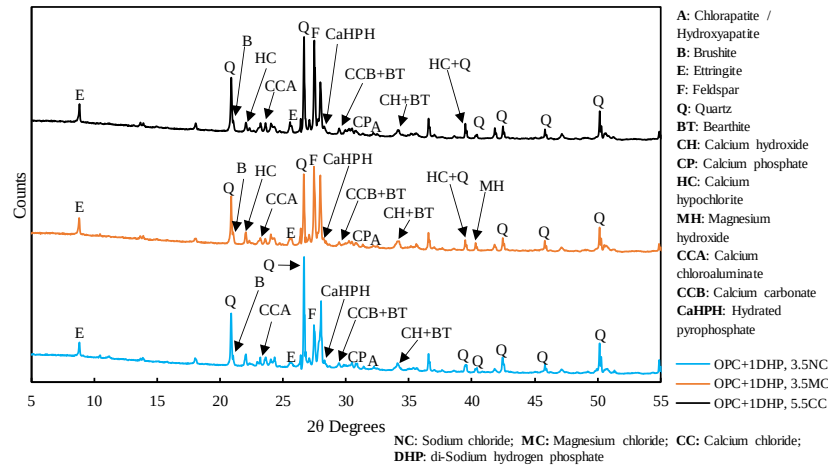


Fig. 6.26 XRD patterns of OPC concrete admixed with 1% DHP at w/c of 0.45, and exposed to different chloride salt solutions

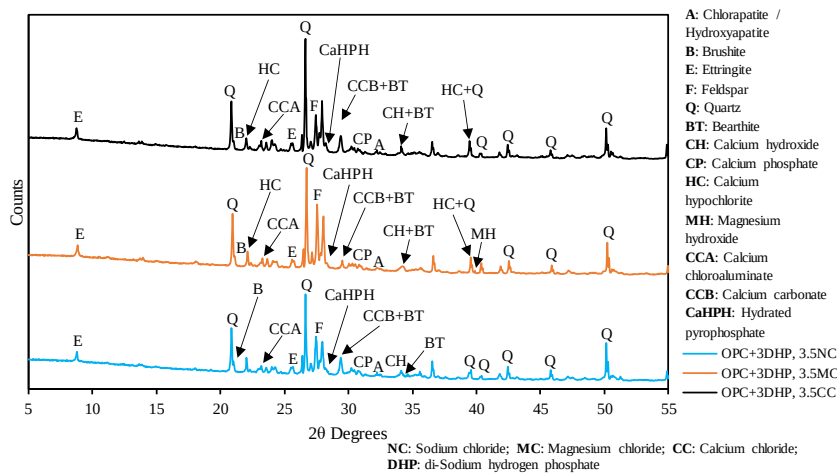


Fig. 6.27 XRD patterns of OPC concrete admixed with 3% DHP at w/c of 0.55, and exposed to different chloride salt solutions

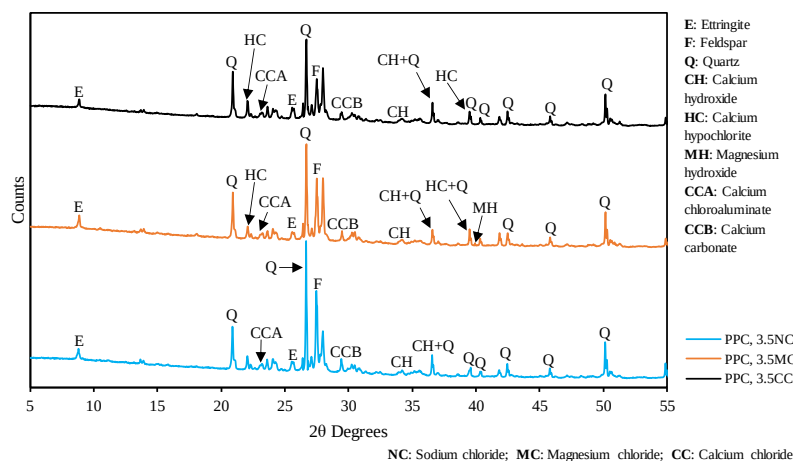


Fig. 6.28 XRD patterns of control concrete made from PPC at w/c of 0.55, and exposed to different chloride salt solutions

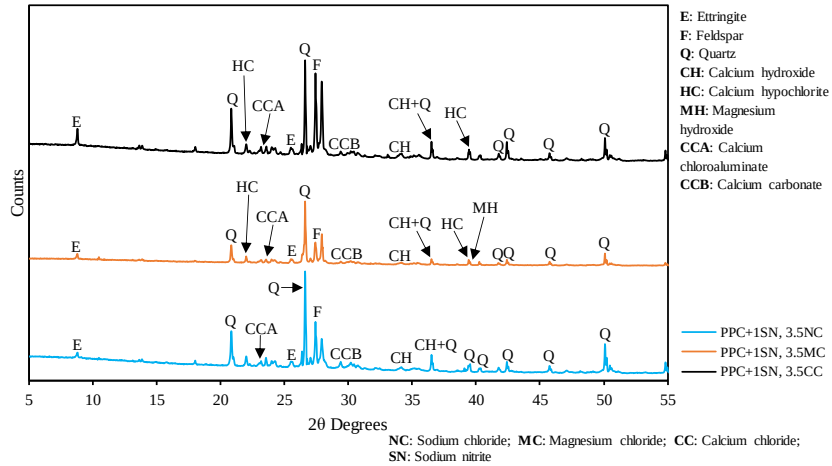


Fig. 6.29 XRD patterns of PPC concrete admixed with 1% NaNO_2 at w/c of 0.45, and exposed to different chloride salt solutions

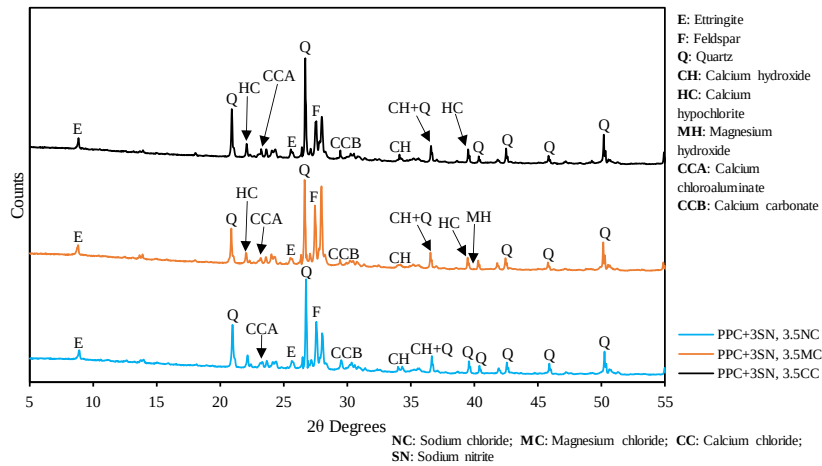


Fig. 6.30 XRD patterns of PPC concrete admixed with 3% NaNO_2 at w/c of 0.55, and exposed to different chloride salt solutions

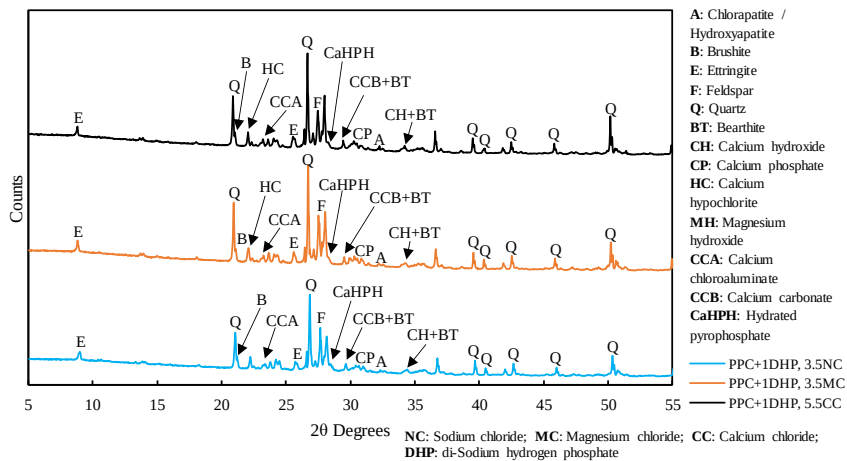


Fig. 6.31 XRD patterns of PPC concrete admixed with 1% DHP at w/c of 0.55, and exposed to different chloride salt solutions

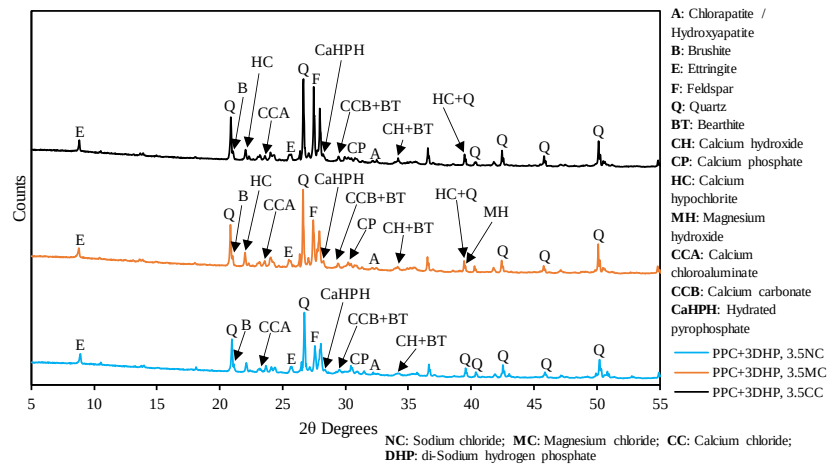


Fig. 6.32 XRD patterns of PPC concrete admixed with 3% DHP at w/c of 0.45, and exposed to different chloride salt solutions

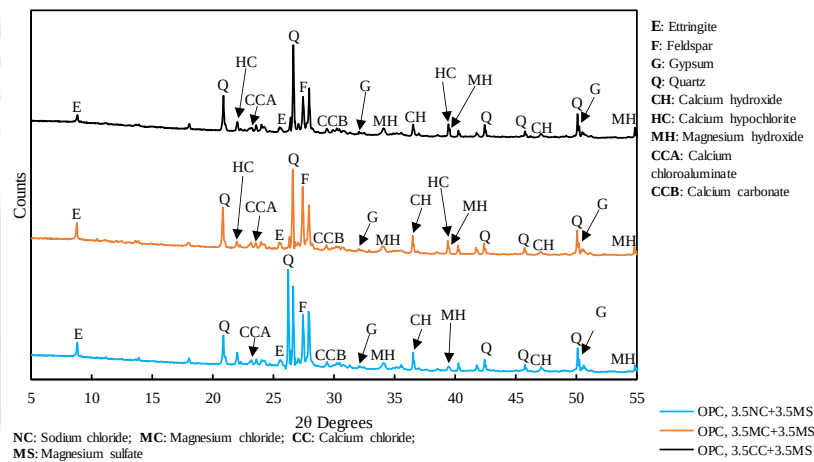


Fig. 6.33 XRD patterns of control concrete made from OPC at w/c of 0.45, and exposed to different composite chloride-sulfate solutions

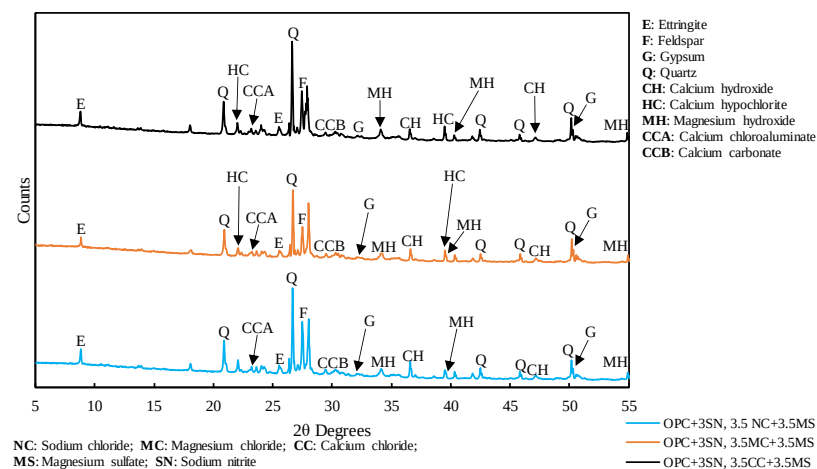


Fig. 6.34 XRD patterns of OPC concrete admixed with 3% NaNO_2 at w/c of 0.45, and exposed to different composite chloride-sulfate solutions

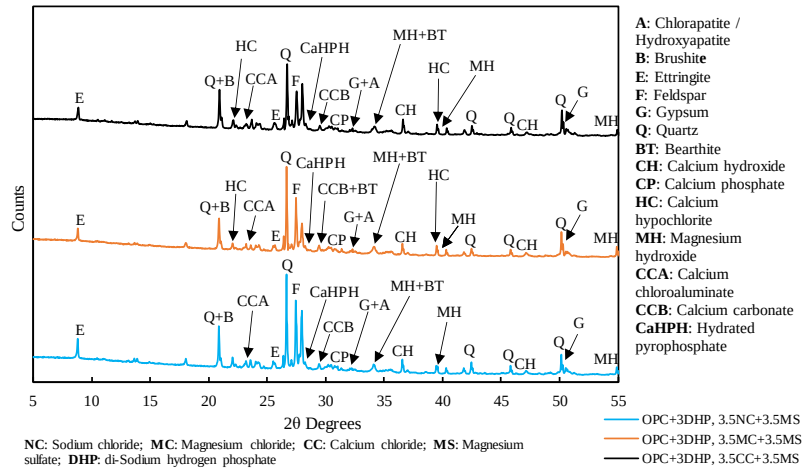


Fig. 6.35 XRD patterns of OPC concrete admixed with 3% DHP at w/c of 0.45, and exposed to different composite chloride-sulfate solutions

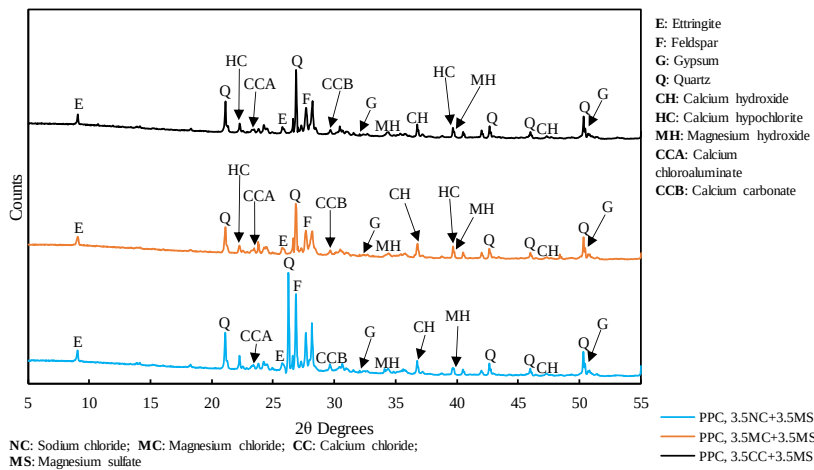


Fig. 6.36 XRD patterns of control concrete made from PPC at w/c of 0.45, and exposed to different composite chloride-sulfate solutions

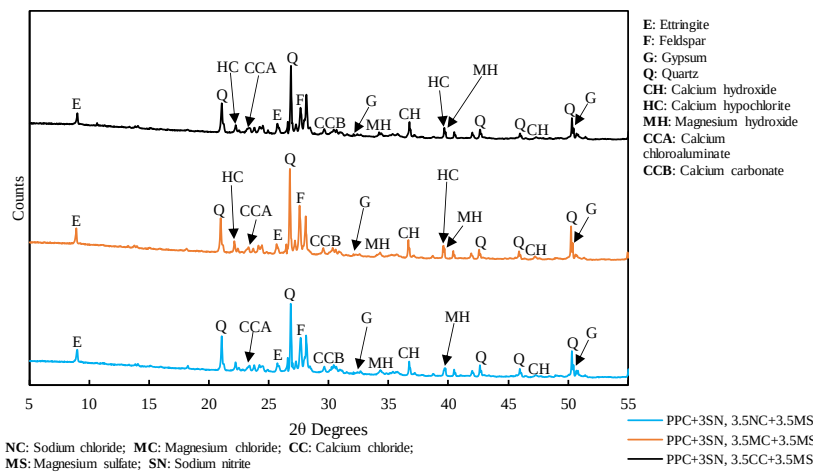


Fig. 6.37 XRD patterns of PPC concrete admixed with 3% NaNO_2 at w/c of 0.45, and exposed to different composite chloride-sulfate solutions

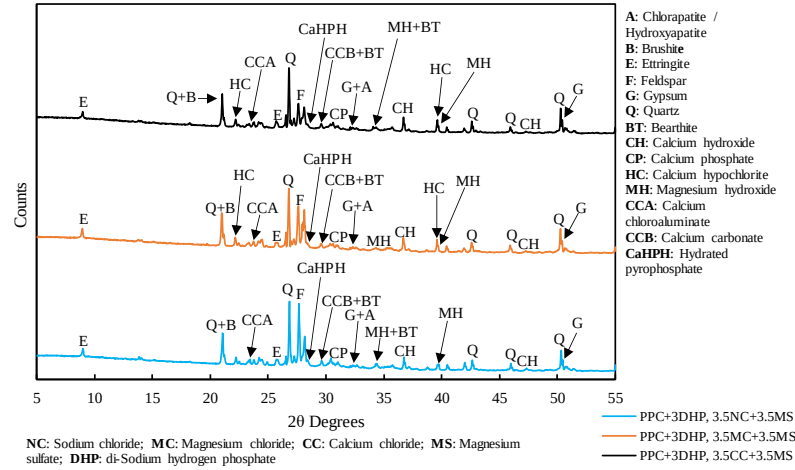


Fig. 6.38 XRD patterns of PPC concrete admixed with 3% DHP at w/c of 0.45, and exposed to different composite chloride-sulfate solutions

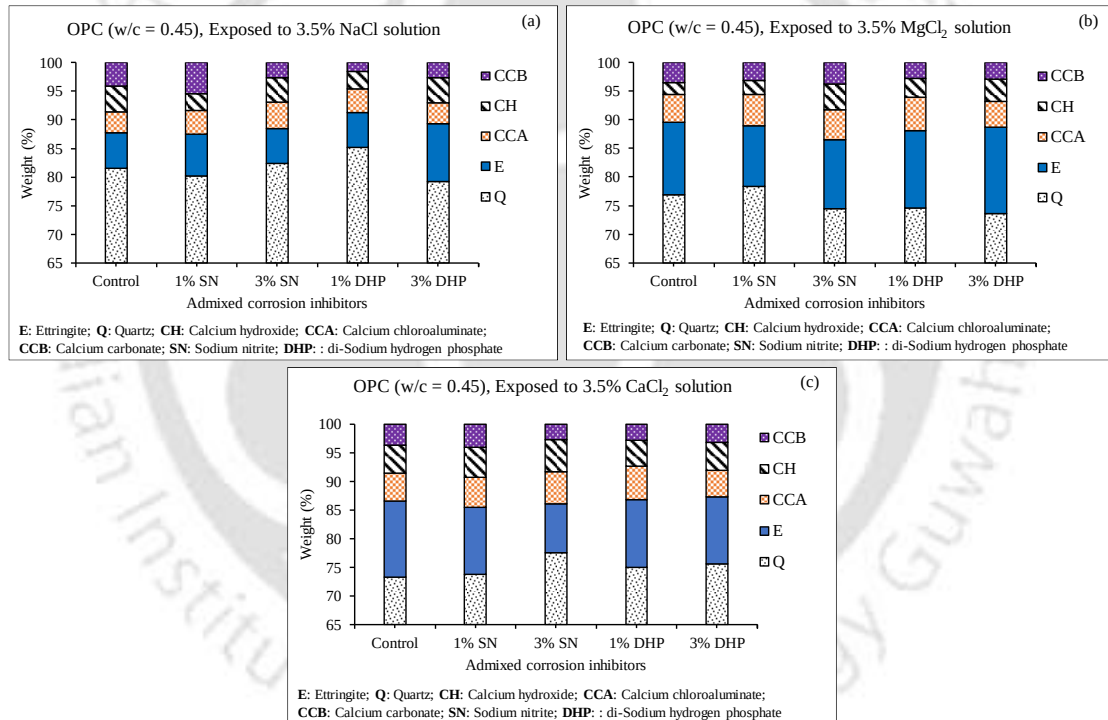


Fig. 6.39 Weight (%) of compounds from XRD patterns of OPC concrete admixed with, and without corrosion inhibitors at w/c of 0.45, and exposed to chloride salt solutions: (a) 3.5% NaCl solution, (b) 3.5% MgCl₂ solution, and (c) 3.5% CaCl₂ solution

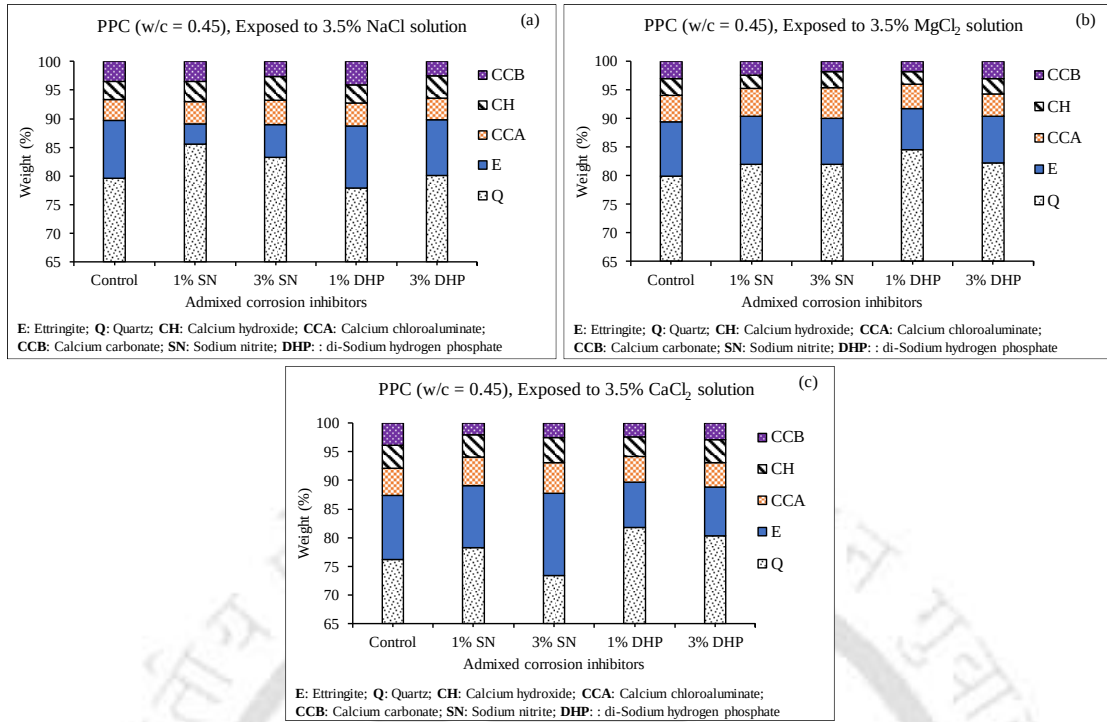


Fig. 6.40 Weight (%) of compounds from XRD patterns of PPC concrete admixed with, and without corrosion inhibitors at w/c of 0.45, and exposed to chloride salt solutions: (a) 3.5% NaCl solution, (b) 3.5% MgCl₂ solution, and (c) 3.5% CaCl₂ solution

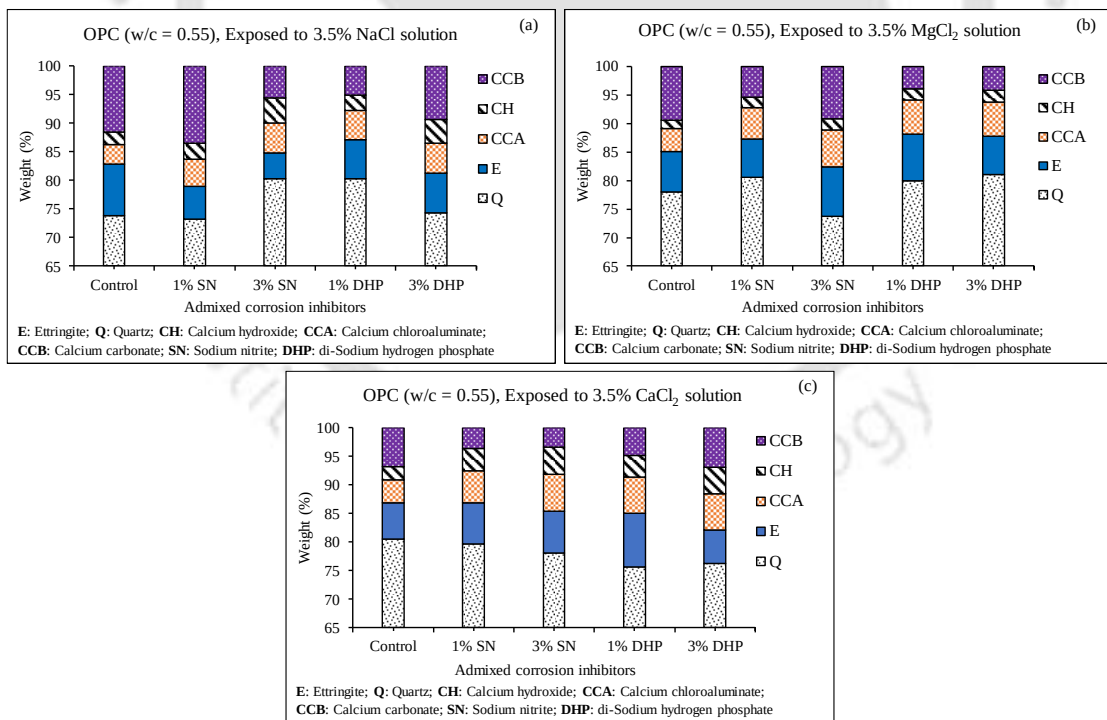


Fig. 6.41 Weight (%) of compounds from XRD patterns of OPC concrete admixed with, and without corrosion inhibitors at w/c of 0.55, and exposed to chloride salt solutions: (a) 3.5% NaCl solution, (b) 3.5% MgCl₂ solution, and (c) 3.5% CaCl₂ solution

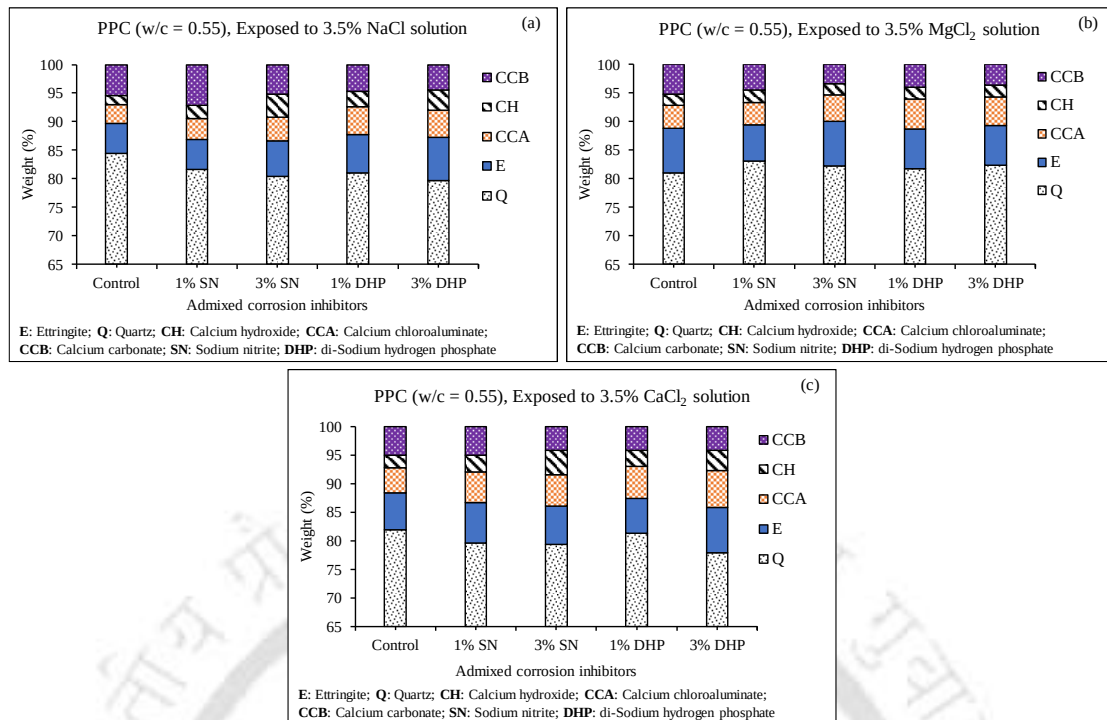


Fig. 6.42 Weight (%) of compounds from XRD patterns of PPC concrete admixed with, and without corrosion inhibitors at w/c of 0.55, and exposed to chloride salt solutions: (a) 3.5% NaCl solution, (b) 3.5% MgCl₂ solution, and (c) 3.5% CaCl₂ solution

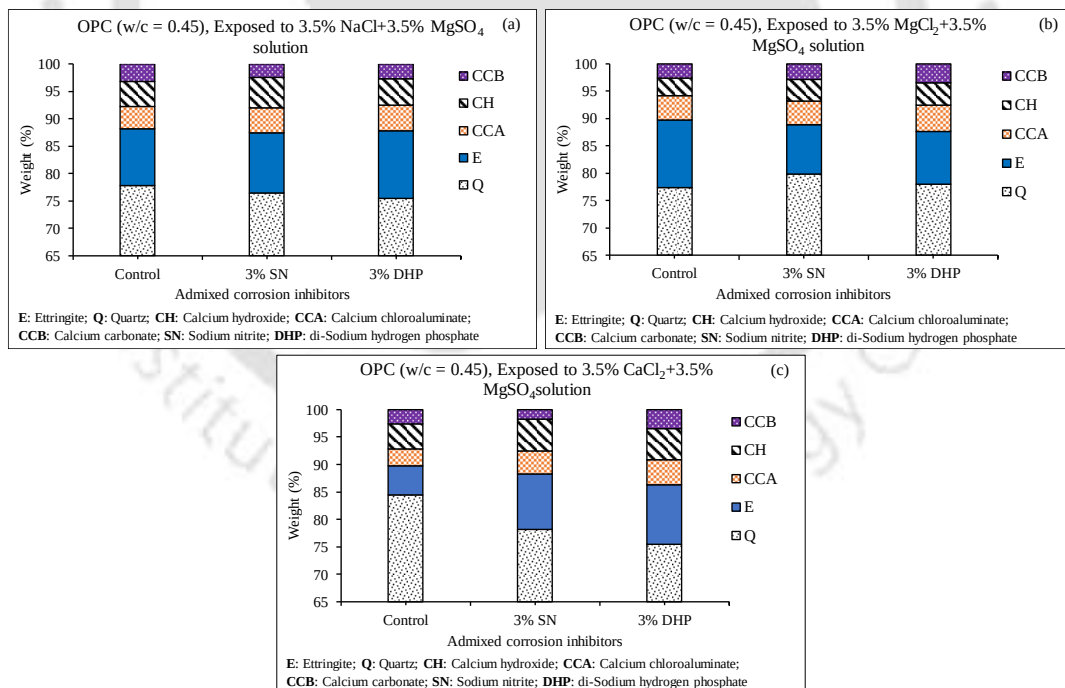


Fig. 6.43 Weight (%) of compounds from XRD patterns of OPC concrete admixed with, and without corrosion inhibitors at w/c of 0.45, and exposed to composite chloride-sulfate solutions: (a) 3.5% NaCl+3.5% MgSO₄ solution, (b) 3.5% MgCl₂+3.5% MgSO₄ solution, and (c) 3.5% CaCl₂+3.5% MgSO₄ solution

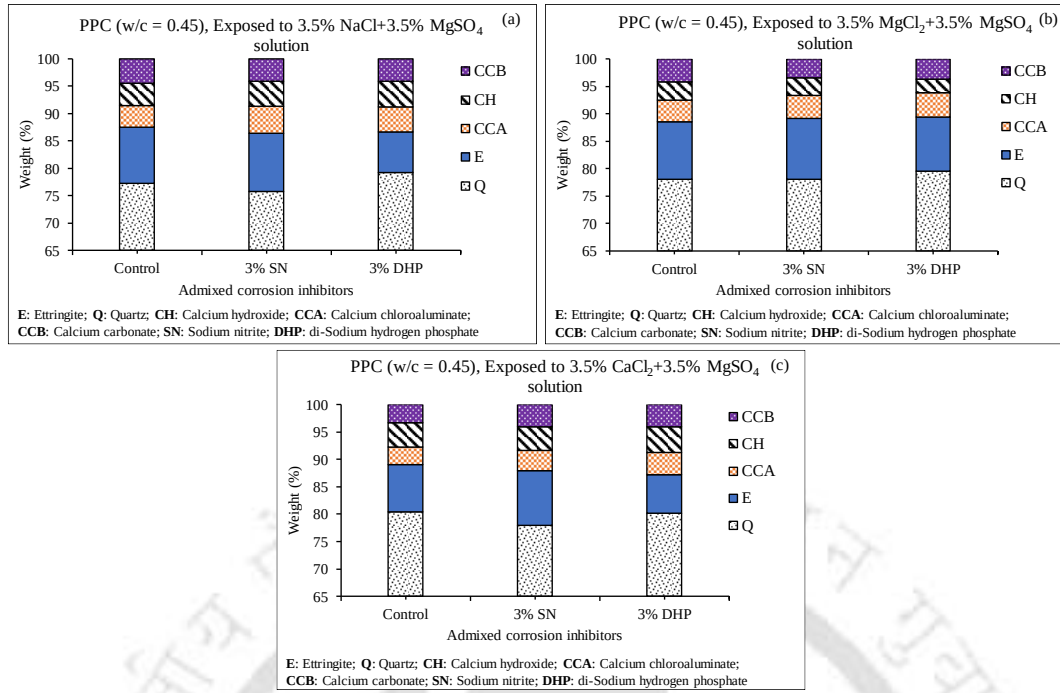


Fig. 6.44 Weight (%) of compounds from XRD patterns of PPC concrete admixed with, and without corrosion inhibitors at w/c of 0.45, and exposed to composite chloride-sulfate solutions: (a) 3.5% NaCl+3.5% MgSO₄ solution, (b) 3.5% MgCl₂+3.5% MgSO₄ solution, and (c) 3.5% CaCl₂+3.5% MgSO₄ solution

From the obtained results of XRD analysis, the variations in the formations of different compounds with cement type, w/c, corrosion inhibitor, and cation type of chloride salt in chloride, and composite chloride-sulfate exposure solutions were analyzed using the peak intensity, and weight (%) of the compounds. From Fig. 6.23 to Fig. 6.38, and Appendix A: Fig. A13 to Fig. A22, the peaks of portlandite (calcium hydroxide, CH) were identified at 34.1° 2θ, and 36.5° 2θ in both OPC, and PPC concrete mixes. The weight (%) of portlandite (CH) was mostly higher in OPC concrete as compared to PPC concrete except for some cases in case of exposure to MgCl₂ solution, and MgCl₂+MgSO₄ solution. The lower amount of portlandite in PPC concrete may be attributed to the pozzolanic activity where calcium hydroxide was consumed in the pozzolanic reaction. In some cases, the lower weight (%) of portlandite (CH) in OPC concrete exposed to MgCl₂, and MgCl₂+MgSO₄ solutions may be attributed to its consumption in the formation of magnesium hydroxide (MH) in the presence of Mg²⁺ ions to a greater extent in OPC concrete than that in PPC concrete. The formation of magnesium hydroxide (brucite) can be observed from the XRD patterns of concrete exposed to MgCl₂ solution, and those exposed to composite chloride-sulfate (NaCl+MgSO₄, MgCl₂+MgSO₄, and CaCl₂+MgSO₄) solutions, where its peak was identified at 39.92° 2θ for both OPC, and PPC concrete, and at both w/c. As observed from

the XRD patterns (Fig. 6.23 to Fig. 6.38, and Appendix A: Fig. A13 to Fig. A22), the peak corresponding to magnesium hydroxide was relatively more intense in OPC concrete than PPC concrete in case of exposure to MgCl_2 solution (for both w/c, i.e., 0.45, and 0.55), and those exposed to composite chloride-sulfate solutions (for w/c of 0.45). While comparing the composite chloride-sulfate solutions, i.e., $\text{NaCl}+\text{MgSO}_4$, $\text{MgCl}_2+\text{MgSO}_4$, and $\text{CaCl}_2+\text{MgSO}_4$ solutions, it is observed that there is no systematic variation in peak intensity of magnesium hydroxide among the composite chloride-sulfate solutions. This may be attributed to the effect of alteration in the extent of reaction of calcium hydroxide with magnesium sulfate in the presence of different cation type of chloride salts in the concrete mixes. Further, the concrete exposed to CaCl_2 solution showed higher weight (%) of portlandite than NaCl solution followed by exposure to MgCl_2 solution irrespective of cement type, w/c, and presence of corrosion inhibitors as observed from Fig. 6.39 to Fig. 6.42. The similar variation in weight (%) of portlandite (calcium hydroxide) was observed among composite chloride-sulfate exposure solutions, i.e., the weight (%) of portlandite was higher in case of exposure to $\text{CaCl}_2+\text{MgSO}_4$ solution than $\text{NaCl}+\text{MgSO}_4$ solution followed by $\text{MgCl}_2+\text{MgSO}_4$ solution as observed from Fig. 6.43, and Fig. 6.44. The presence of higher amount of calcium hydroxide (CH) in the concrete exposed to CaCl_2 , and $\text{CaCl}_2+\text{MgSO}_4$ solutions as indicated from the XRD analysis may be due to the fact that the ingress of CaCl_2 decreases the leaching velocity of calcium hydroxide [37], and increased its formation as a result of reaction of calcium ions from CaCl_2 with the hydroxyl ions present in the pore solution of concrete. The reason behind lower portlandite content in the concrete exposed to MgCl_2 solution (irrespective of presence of MgSO_4) than those exposed to other two chloride solutions, and their corresponding composite solutions is due to its consumption in the formation of brucite (as stated earlier), and calcium hypochlorite (HC). The formation of calcium hypochlorite in OPC, and PPC concrete mixes exposed to MgCl_2 , and CaCl_2 solutions (for w/c of 0.45, and 0.55), and those exposed to $\text{MgCl}_2+\text{MgSO}_4$ and $\text{CaCl}_2+\text{MgSO}_4$ solutions (for w/c of 0.45) was confirmed through its peaks observed at $21.7^\circ 2\theta$, and $39.4^\circ 2\theta$ in the XRD patterns as shown in Fig. 6.23 to Fig. 6.38, and Appendix A: Fig. A13 to Fig. A22. The peaks corresponding to calcium hypochlorite (HC) were mostly more intense in the concrete exposed to MgCl_2 solution than that exposed to CaCl_2 solution irrespective of presence of MgSO_4 in the exposure solutions. Further, the peak intensity of calcium hypochlorite was mostly higher in the concrete made with w/c of 0.55 as compared to 0.45 irrespective of cement type, presence of corrosion inhibitors, and chloride exposure solution (i.e., MgCl_2 , and CaCl_2). The

formation of higher amount of calcium hypochlorite in the concrete made with higher w/c may be due to the effect of ingress of more amount of chloride ions at higher w/c as compared to that at lower w/c. From the obtained weight (%) of calcium hydroxide (CH), it is observed that there is no systematic variation in the amount of calcium hydroxide between control mix, and those admixed with corrosion inhibitors for both OPC, and PPC, and for all chloride exposure solutions at w/c of 0.45. The unsystematic variation in the amount of calcium hydroxide between control concrete, and those admixed with corrosion inhibitors may be attributed the effect of alteration in its leaching in the presence of chloride ions. However, at w/c of 0.55, the amount of calcium hydroxide was mostly higher in the concrete admixed with corrosion inhibitors than control mix irrespective of cement type, and chloride exposure solution. Similarly, in case of exposure to composite chloride-sulfate solutions, the weight (%) of calcium hydroxide was mostly lower in the control concrete than those admixed with corrosion inhibitors at w/c of 0.45. The lower amount of calcium hydroxide (portlandite) in the control mix may be attributed to the effect of its leaching to a greater extent in the presence of higher amount of chloride ions. As stated earlier, the ingress of chloride ions was more in the control concrete thereby resulting in higher free chloride ion content as compared to the concrete admixed with corrosion inhibitors. The DHP admixed concrete mostly showed lower calcium hydroxide (CH) content as compared to NaNO_2 admixed concrete as observed from its weight (%) shown in Fig. 6.39 to Fig. 6.44, in both chloride, and composite chloride-sulfate solutions. The consumption of calcium hydroxide (CH) in the formation of phosphate based compounds in the presence of phosphate ions resulted in lower calcium hydroxide content in the concrete containing DHP. The addition of DHP in the concrete mixes resulted in the formation of phosphate based compounds such as calcium phosphate identified at $27.76^\circ 2\theta$ and $31.02^\circ 2\theta$; and chlorapatite/hydroxyapatite at $32.29^\circ 2\theta$ as observed from the XRD patterns shown in Fig. 6.26, Fig. 6.27, Fig. 6.31, Fig. 6.32, Fig. 6.35, Fig. 6.38, and Appendix A: Fig. A16, Fig. A17, Fig. A21, and Fig. A22. In addition, the peaks of brushite, hydrated pyrophosphate, and bearthite were identified at $20.94^\circ 2\theta$; $28.4^\circ 2\theta$; and $29.2^\circ 2\theta$, and $34.9^\circ 2\theta$ respectively in the concrete containing DHP as observed from the XRD patterns shown in Fig. 6.26, Fig. 6.27, Fig. 6.31, Fig. 6.32, Fig. 6.35, Fig. 6.38, and Appendix A: Fig. A16, Fig. A17, Fig. A21, and Fig. A22. Further, mostly more intense peaks of bearthite, and chlorapatite/hydroxyapatite were observed in the XRD patterns (Fig. 6.26, Fig. 6.27, Fig. 6.31, Fig. 6.32, and Appendix A: Fig. A16, Fig. A17, Fig. A21, and Fig. A22) at higher dosage of DHP (i.e., 3%) as compared to lower dosage of DHP (i.e., 1%). As observed

from Fig. 6.39 to Fig. 6.42, the weight (%) of calcium hydroxide (CH) in concrete increased with increase in dosage of both the corrosion inhibitors in case of exposure to chloride solutions. The lower calcium hydroxide content at lower dosage of inhibitors may be ascribed to the leaching of calcium hydroxide to a higher extent in the presence of higher chloride content as there was penetration of more amount of chloride ions leading to higher free chloride ion content at lower dosage of inhibitors as compared to higher dosage of inhibitors (as observed from free chloride ion content shown in Fig. 6.17 (b, c, d, e), Fig. 6.18 (b, c, d, e), Fig. 6.19 (b, c, d, e), and Fig. 6.20 (b, c, d, e)). While analyzing the effect of sulfate ion on calcium hydroxide content, it is observed that the weight (%) of calcium hydroxide was mostly lower in the concrete exposed to composite chloride-sulfate solutions than that exposed to only chloride solutions irrespective of cement type, presence of corrosion inhibitors, and chloride salt in the exposure solutions (Fig. 6.39, Fig. 6.40, Fig. 6.43, and Fig. 6.44). This may be attributed to the effect of MgSO_4 attack wherein the MgSO_4 reacts with calcium hydroxide, and results in the formation of magnesium hydroxide (brucite) thereby lowering the calcium hydroxide content in the concrete exposed to composite chloride-sulfate solutions as compared to chloride solutions. While comparing the effect of w/c on weight (%) of calcium hydroxide (CH), it is observed that the weight (%) of calcium hydroxide was mostly lower in the concrete prepared with w/c of 0.55 than that prepared with w/c of 0.45 irrespective of cement type, presence of corrosion inhibitors, and chloride exposure solutions (Fig. 6.39 to Fig. 6.42). The lower amount of calcium hydroxide in the concrete made with w/c of 0.55 may be attributed to the presence of higher amount of chloride ions that resulted in leaching of calcium hydroxide to a comparatively greater extent as compared to that in the concrete made with w/c of 0.45.

The presence of ettringite (E) in the concrete mixes is confirmed by its peaks observed at $8.8^\circ 2\theta$, and $25.6^\circ 2\theta$ in the XRD patterns shown in Fig. 6.23 to Fig. 6.38, and Appendix A: Fig. A13 to Fig. A22. The weight (%) of ettringite obtained from the XRD patterns was mostly higher in OPC concrete than PPC concrete irrespective of w/c, presence of corrosion inhibitors, and type of exposure solution (both chloride, and composite chloride-sulfate solutions) as observed from Fig. 6.39 to Fig. 6.44. The higher amount of ettringite in OPC concrete than PPC concrete may be attributed to the reaction of gypsum with C_3A in case of exposure to chloride solutions, and dominant effect of reaction of sulfate ions with C_3A in case of exposure to composite chloride-sulfate solutions to a comparatively greater

extent. Further, in the concrete exposed to only chloride solutions, there was no systematic variation in weight (%) of ettringite with cation type of chloride salt in the exposure solution, and dosage of corrosion inhibitors. However, the weight (%) of ettringite was mostly higher in the concrete admixed with DHP as compared to NaNO_2 irrespective of cement type, w/c, and chloride exposure solutions. The lower amount of ettringite in the concrete containing NaNO_2 may be due to the effect of solubility of ettringite in the presence of chloride to a higher extent as a result of penetration of more amount of chloride ions into the concrete containing NaNO_2 than that containing DHP. It may be noted that the free chloride ion content was higher in the concrete containing NaNO_2 than that containing DHP in case of exposure to chloride solutions (Fig. 6.17 (b, c, d, e), Fig. 6.18 (b, c, d, e), Fig 6.19 (b, c, d, e), and Fig. 6.20 (b, c, d, e)). In case of concrete exposed to composite chloride-sulfate solutions, there was unsystematic variation in weight (%) of ettringite with cation type of chloride salt, and type of corrosion inhibitor. The unsystematic variation in amount of ettringite with cation type of chloride salt in the composite chloride-sulfate solutions may be attributed to the effect of alterations in the extent of reaction of sulfate ions with C_3A in the concomitant presence of different cation type of chloride salts. Further, the unsystematic variation in amount of ettringite with type of corrosion inhibitor in case of exposure to composite chloride-sulfate solutions may be ascribed to the effect of variations in the solubility of ettringite in the presence of chloride ions. It may be noted that there was no systematic variation in the free chloride ion content between DHP, and NaNO_2 in the concrete exposed to composite chloride-sulfate solutions. The weight (%) of ettringite was mostly higher in the concrete exposed to composite chloride-sulfate solutions as compared to that exposed to only chloride solutions irrespective of cement type, presence of corrosion inhibitors, and chloride salt in the exposure solutions. The presence of higher amount of ettringite in the concrete exposed to composite chloride-sulfate solutions is due to the effect of preferential reaction of sulfate ions over chloride ions with C_3A . The presence of lower amount of ettringite in the concrete exposed to only chloride solutions may be attributed to the effect of solubility of ettringite to a greater extent in the presence of chloride ions. The amount of ettringite was mostly lower in the concrete made with w/c of 0.55 than that made with w/c of 0.45 irrespective of cement type, presence of corrosion inhibitors, and chloride exposure solutions as observed from the weight (%) of ettringite shown in Fig. 6.39 to Fig. 6.42. The presence of lower amount of ettringite in the concrete made with higher w/c may be due to the effect of its solubility to a higher extent as a result

of presence of more amount of chloride ions in the concrete made with w/c of 0.55 than that made with w/c of 0.45.

In all the XRD patterns (Fig. 6.23 to Fig. 6.38, and Appendix A: Fig. A13 to Fig. A22), irrespective of cement type, w/c, presence of corrosion inhibitors, and exposure solution (both chloride, and composite chloride-sulfate solutions), the presence of calcium chloroaluminate (CCA) in concrete is confirmed through its peaks identified at $11.2^\circ 2\theta$, and $23.2^\circ 2\theta$. The obtained weight (%) from the semi-quantification analysis showed that calcium chloroaluminate (Friedel's salt) formation is more in OPC concrete than PPC concrete (Fig. 6.39 to Fig. 6.44) for all exposure solutions. This is due to the effect of reaction of C_3A with chloride ions to a higher extent due to more C_3A content in OPC than PPC, which is in line with the variation in the obtained bound chloride ion (C_B) content between two cements. In case of concrete exposed to only chloride solutions, the formation of calcium chloroaluminate was more in the concrete exposed to $CaCl_2$ solution as compared to other chloride solutions (Fig. 6.39 to Fig. 6.42), which is ascribed to the effect of comparatively greater extent of reaction between chloride ions, and C_3A in the concrete subjected to $CaCl_2$ solution. Further, the concrete exposed to $NaCl$ solution showed less amount of calcium chloroaluminate than $MgCl_2$ solution as observed from the results of XRD analysis, which may be attributed to the effect of decomposition of calcium chloroaluminate at higher alkalinity of pore solution in the presence of sodium ions in the concrete exposed to $NaCl$ solution. In case of concrete exposed to composite chloride-sulfate solutions, the calcium chloroaluminate content was lower in the concrete subjected to $CaCl_2+MgSO_4$ solution as compared to $MgCl_2+MgSO_4$ followed by $NaCl+MgSO_4$ solutions as observed from its weight (%) shown in Fig. 6.43, and Fig. 6.44. The reason behind lower calcium chloroaluminate content in the concrete exposed to $CaCl_2+MgSO_4$ solution as compared to other composite chloride-sulfate solution was explained earlier in Section 6.3. The higher calcium chloroaluminate content in the concrete subjected to $NaCl+MgSO_4$ solution as compared to $MgCl_2+MgSO_4$ solution may be attributed to the dominant effect of penetration of more amount of chloride ions into the concrete exposed to $NaCl+MgSO_4$ solution that resulted in reaction of chloride ions with C_3A to a greater extent. The variations in the formation of calcium chloroaluminate in the concrete as observed from the results of XRD analysis are in line with the variations in the observed bound chloride ion contents (discussed earlier) among different chloride, and composite chloride-sulfate solutions. Further, the addition of corrosion inhibitors favoured the

formation of calcium chloroaluminate as its obtained weight (%) was higher in the concrete admixed with corrosion inhibitors as compared to control concrete for all exposure solutions, i.e., chloride, and composite chloride-sulfate solutions (Fig. 6.39 to Fig. 6.44). From Fig. 6.39 to Fig. 6.42, it is observed that, in case of concrete exposed to only chloride solutions, at 1% inhibitor dosage, the weight (%) of calcium chloroaluminate was mostly higher in the concrete containing DHP than NaNO_2 , whereas at 3% dosage, mostly the opposite variation was observed in the weight (%) of calcium chloroaluminate. At 1% dosage, the higher calcium chloroaluminate content in the concrete containing DHP may be ascribed to the dominant effect of reaction of chloride ions with C_3A to a greater extent over the effect of partial replacement of NO_2^- ions from nitrite-AFm by chloride ions to a lower extent in the concrete containing sodium nitrite. Similarly, at 3% dosage, the higher calcium chloroaluminate content in the concrete containing sodium nitrite may be attributed to the significant effect of partial replacement of NO_2^- ions from nitrite-AFm by chloride ions over the effect of lower formation of calcium chloroaluminate in the concrete containing DHP. Further, the formation of calcium chloroaluminate mostly decreased with increase in dosage of DHP whereas the opposite variation was observed in case of NaNO_2 as observed from the results of XRD analysis. The formation of lower amount of calcium chloroaluminate at higher dosage (3%) of DHP is attributed to the significant effect of formation of comparatively more amount of chlorapatite (as observed from the XRD patterns) at higher dosage of DHP thereby resulting in availability of lower amount of chloride ions to react with C_3A as compared that at lower dosage (1%) of DHP. At 3% dosage of NaNO_2 , the presence of more amount of nitrite-AFm resulted in the formation of higher amount of Friedel's salt (due to partial replacement of NO_2^- ions from nitrite-AFm by chloride ions, as stated earlier) even though the free chloride ion content was lower at higher dosage (3%) of NaNO_2 than that at lower dosage (1%). In case of concrete exposed to composite chloride-sulfate solutions, the weight (%) of calcium chloroaluminate (CCA) was mostly higher in the concrete containing DHP than that containing NaNO_2 (at 3% dosage) irrespective of cement type, and type of chloride salt in the exposure solution as evident from Fig. 6.43, and Fig. 6.44. This may be attributed the effect of reaction of chloride ions with C_3A to a comparatively higher extent in the concrete containing DHP than that containing sodium nitrite in the concomitant presence of sulfate ions. While comparing between chloride solutions, and composite chloride-sulfate solutions, the weight (%) of calcium chloroaluminate was lower in the concrete exposed to composite chloride-

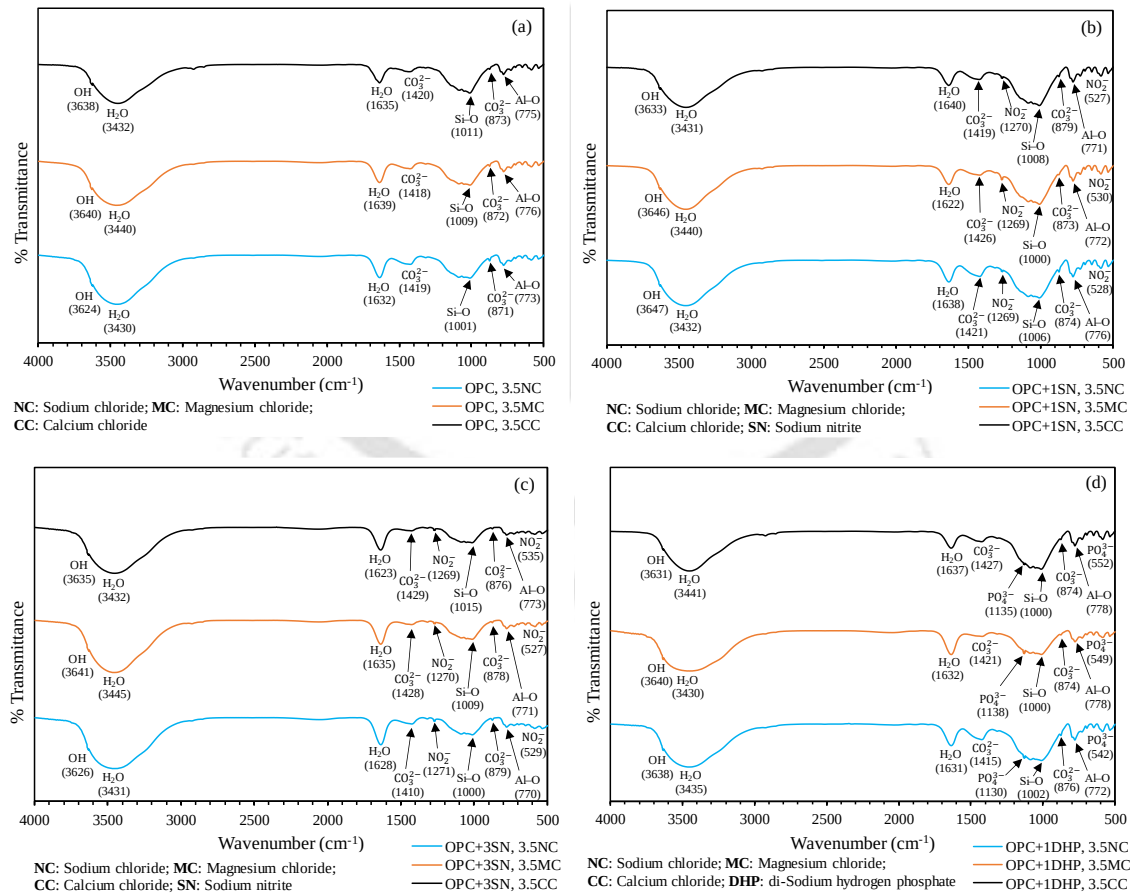
sulfate solutions than that exposed to only chloride solutions irrespective of cement type, presence of corrosion inhibitors, and type of chloride salt in the exposure solutions. The presence of lower amount of calcium chloroaluminate in the concrete exposed to composite chloride-sulfate solutions may be attributed to effect of conversion of calcium chloroaluminate to ettringite in the presence of sulfate ions [190] as well as lower extent of reaction of chloride ions with C_3A due to ingress of lower amount of chloride ions into the concrete exposed to composite chloride-sulfate solutions as compared to that exposed to only chloride solutions. While comparing the effect of w/c, the weight (%) of calcium chloroaluminate was mostly higher in the concrete prepared with w/c of 0.55 than that prepared with w/c of 0.45 irrespective of cement type, presence of corrosion inhibitors, and chloride exposure solution. The reason behind this is attributed to the effect of reaction of chloride ions with C_3A to a higher extent in the concrete made with w/c of 0.55 (due to ingress of more amount of chloride ions) than that made with w/c of 0.45.

From Fig. 6.33 to Fig. 6.38, the peaks of gypsum (G) in the concrete exposed to composite chloride-sulfate solutions were observed at $32.1^\circ 2\theta$, and $50.5^\circ 2\theta$ in the obtained XRD patterns. The peak intensity of gypsum (G) was mostly higher in PPC concrete than OPC concrete irrespective of presence of corrosion inhibitors, and cation type of chloride salt in the composite chloride-sulfate exposure solution. The presence of higher amount of gypsum in PPC concrete may be attributed to its lower consumption in the formation of ettringite in the presence of sulfate ions as compared to OPC concrete. It may be noted that as discussed earlier (from results of XRD analysis), the amount of ettringite was mostly lower in PPC concrete as compared to OPC concrete. Further, the variation in peak intensity of gypsum was not systematic with cation type of chloride salt in the composite chloride-sulfate solutions. This may be attributed to the effect of variations in the extent of reaction of sulfate ions with calcium hydroxide in the concomitant presence of chloride ions associated with different cations. The concrete admixed with corrosion inhibitors mostly showed higher peak intensity of gypsum (G) as compared to control concrete as evident from the XRD patterns shown in Fig. 6.33 to Fig. 6.38. The lower amount of calcium hydroxide in control concrete as compared to that admixed with corrosion inhibitors may be the reason behind lower formation of gypsum in control concrete. It may be noted that the calcium hydroxide content was mostly lower in the control concrete as compared to that admixed with corrosion inhibitors as observed from the results of XRD analysis (discussed earlier). Further, there was no systematic variation in peak intensity of gypsum between

NaNO₂, and DHP irrespective of cement type, and composite chloride-sulfate solutions as observed from Fig. 6.34, Fig. 6.35, Fig. 6.37, and Fig. 6.38. This indicates alterations in the extent of reaction of sulfate ions with calcium hydroxide in the presence of corrosion inhibitors in the concrete exposed to composite chloride-sulfate solutions. The peaks of quartz (Q) were observed at 20.8° 2 θ , 26.64° 2 θ , 39.45° 2 θ , 42.45° 2 θ , 45.5° 2 θ , and 50.2° 2 θ in the XRD patterns for both OPC, and PPC concrete exposed to chloride, and composite chloride-sulfate solutions (Fig. 6.23 to Fig. 6.38, and Appendix A: Fig. A13 to Fig. A22). In addition, the peaks of feldspar (F), and calcium carbonate (CaCO₃, CCB) were identified at 27.5° 2 θ , and 29.4° 2 θ respectively in all the XRD patterns.

6.4.2 Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of concrete mixes prepared at w/c of 0.55, and exposed to only chloride solutions are shown in Fig. 6.45, and Fig. 6.46. Similarly, the FTIR spectra of concrete mixes prepared at w/c of 0.45, and exposed to composite chloride-sulfate solutions are shown in Fig. 6.47, and Fig. 6.48.



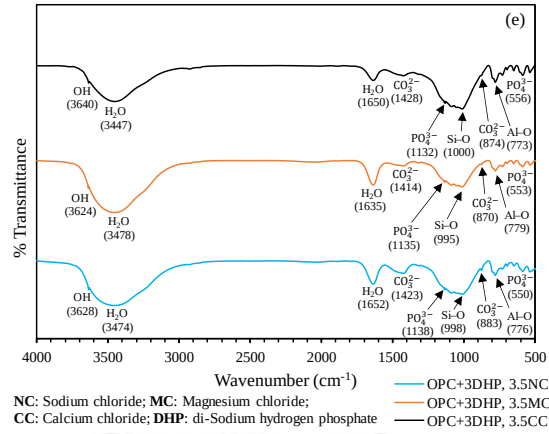
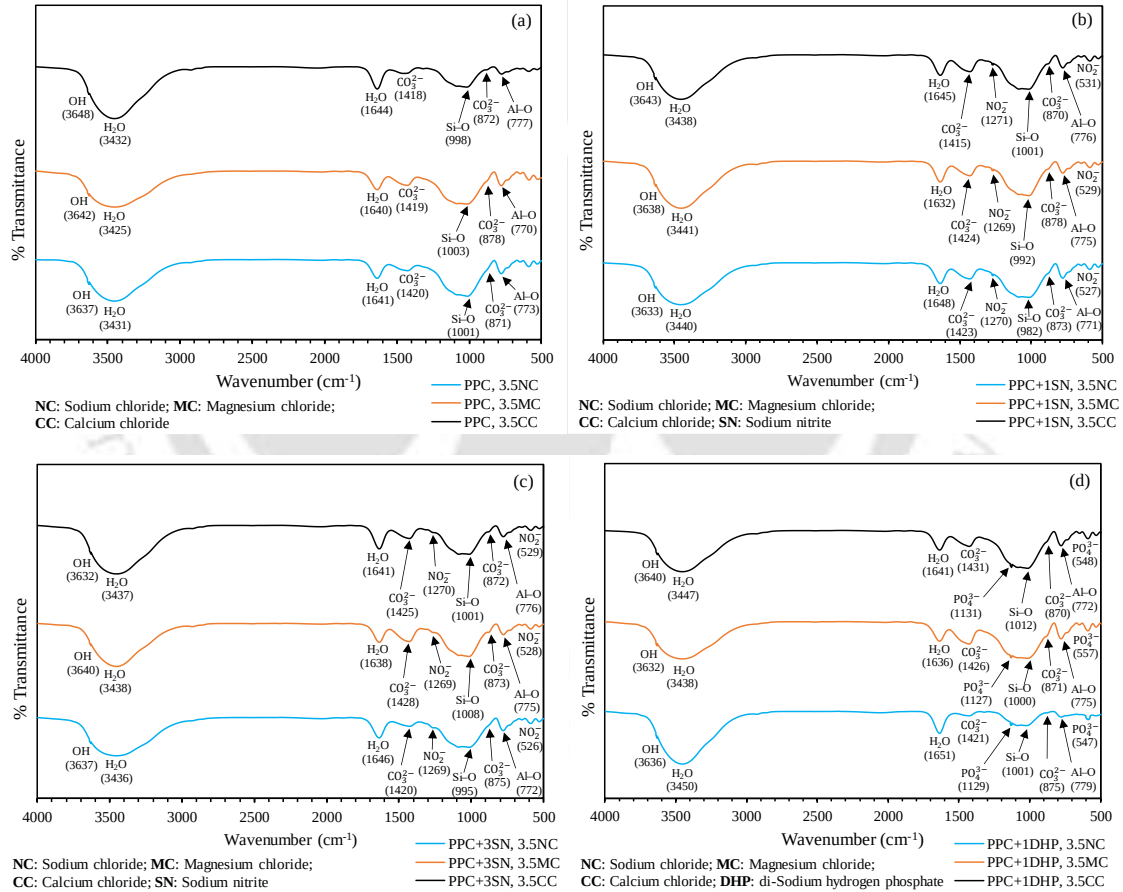


Fig. 6.45 FTIR spectra of OPC concrete at w/c of 0.55, and exposed to 3.5% chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂): (a) control mix, (b) concrete admixed with 1% NaNO₂, (c) concrete admixed with 3% NaNO₂, (d) concrete admixed with 1% DHP, and (e) concrete admixed with 3% DHP



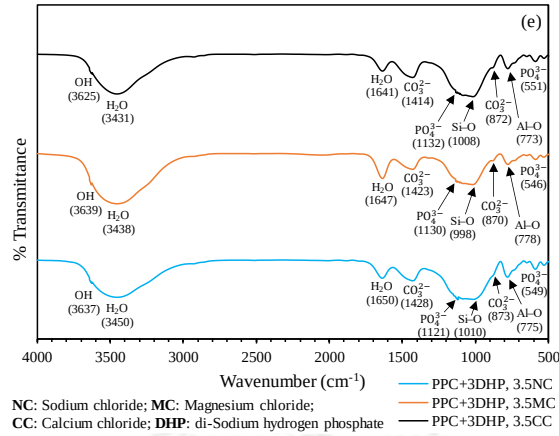


Fig. 6.46 FTIR spectra of PPC concrete at w/c of 0.55, and exposed to 3.5% chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂): (a) control mix, (b) concrete admixed with 1% NaNO₂, (c) concrete admixed with 3% NaNO₂, (d) concrete admixed with 1% DHP, and (e) concrete admixed with 3% DHP

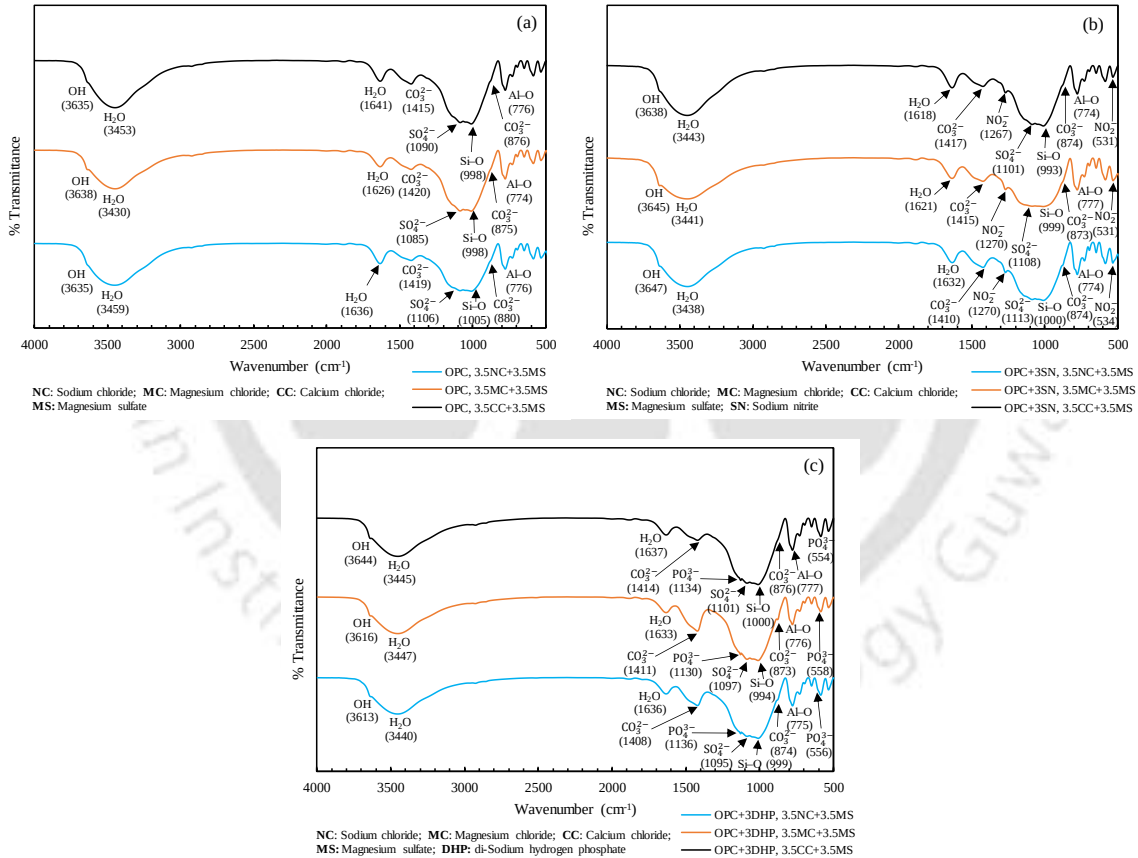


Fig. 6.47 FTIR spectra of OPC concrete at w/c of 0.45, and exposed to composite chloride-sulfate solutions: (a) control mix, (b) concrete admixed with 3% NaNO₂, and (c) concrete admixed with 3% DHP

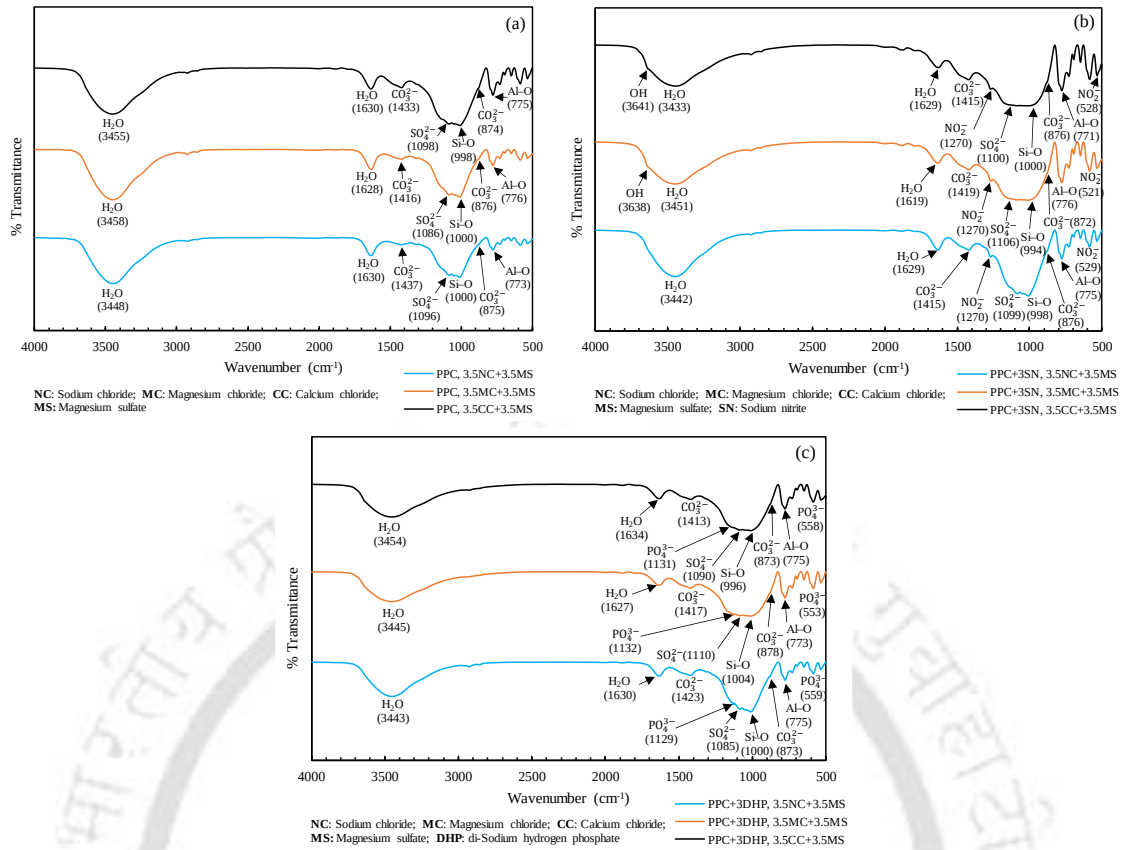


Fig. 6.48 FTIR spectra of PPC concrete at w/c of 0.45, and exposed to composite chloride-sulfate solutions: (a) control mix, (b) concrete admixed with 3% NaNO₂, and (c) concrete admixed with 3% DHP

The band assignment obtained from the FTIR spectra is presented in Table 6.1 [173, 178, 191, 192]. From the FTIR spectra shown in Fig. 6.45 to Fig. 6.48, the compounds formed in concrete were identified using the associated functional groups. In both OPC, and PPC concrete, the presence of calcium hydroxide was confirmed through the stretching vibration of O-H band appeared in the range of 3613 - 3648 cm⁻¹. Similarly, the presence of calcium carbonate in OPC and PPC concrete mixes is confirmed from the bands appeared in the range of 1408 - 1437 cm⁻¹, and 870 - 883 cm⁻¹. Further, in all the concrete mixes, the peaks in the range of 982 - 1016 cm⁻¹ are associated with Si-O asymmetric stretching vibration of calcium silicate hydrate (C-S-H), and the peaks in the range of 770 - 779 cm⁻¹ are related to ettringite. In Fig. 6.45 (b, c), Fig. 6.46 (b, c), Fig. 6.47 (b), and Fig. 6.48 (b), the asymmetric stretching vibration, and bending vibration of nitrite in the range of 1267 - 1271 cm⁻¹, and 621 - 636 cm⁻¹ respectively indicate the formation of nitrite-AFm in the concrete admixed with NaNO₂ irrespective of cement type, and exposure solution. Similarly, in Fig. 6.45 (d, e), Fig. 6.46 (d, e), Fig. 6.47 (c), and Fig. 6.48 (c), the peaks appeared in the range of 1121 - 1138 cm⁻¹, and 642 - 669 cm⁻¹ are attributed to the presence of phosphate based

compounds in the concrete containing DHP. Further, in Fig. 6.47, and Fig. 6.48, the fingerprint peaks appeared in the range of 1098 - 1117 cm^{-1} are associated with the asymmetric stretching vibration of SO_4^{2-} group indicating the presence of gypsum, and ettringite phases [47, 62] in the concrete mixes exposed to composite chloride-sulfate solutions.

Table 6.1. FTIR identification of concrete mixes

Wavenumber (cm^{-1})		Band assignment
OPC concrete	PPC concrete	
3613 - 3647 cm^{-1}	3626 - 3648 cm^{-1}	O–H stretching vibration corresponding to $\text{Ca}(\text{OH})_2$
3430 - 3478 cm^{-1}	3426 - 3468 cm^{-1}	O–H stretching vibration of structural water present in hydration product of cement
1618 - 1662 cm^{-1}	1619 - 1661 cm^{-1}	O–H bending vibration of interlayer water present in hydration product of cement
1408 - 1429 cm^{-1}	1413 - 1437 cm^{-1}	ν_3 vibration of CO_3^{2-}
993 - 1016 cm^{-1}	982 - 1012 cm^{-1}	Si–O asymmetric stretching vibration of calcium silicate hydrate (C–S–H)
871 - 883 cm^{-1}	870 - 878 cm^{-1}	ν_2 vibration of CO_3^{2-}
770 - 779 cm^{-1}	770 - 779 cm^{-1}	Al–O bands of ettringite
1267 - 1271 cm^{-1}	1269 - 1271 cm^{-1}	N–O asymmetric stretching vibration
627 - 636 cm^{-1}	621 - 631 cm^{-1}	O–N–O bending vibration
1130 - 1138 cm^{-1}	1121 - 1132 cm^{-1}	P=O stretching
642 - 668 cm^{-1}	646 - 669 cm^{-1}	P–OH out of plane bending
1086 - 1113 cm^{-1}	1086 - 1110 cm^{-1}	asymmetric stretching vibration of SO_4^{2-}

6.4.3 Field emission scanning electron microscope (FESEM) analysis

Typical FESEM images of concrete admixed with, and without corrosion inhibitors, and exposed to different chloride, and composite chloride-sulfate solutions are shown in Fig. 6.49 to Fig. 6.52.

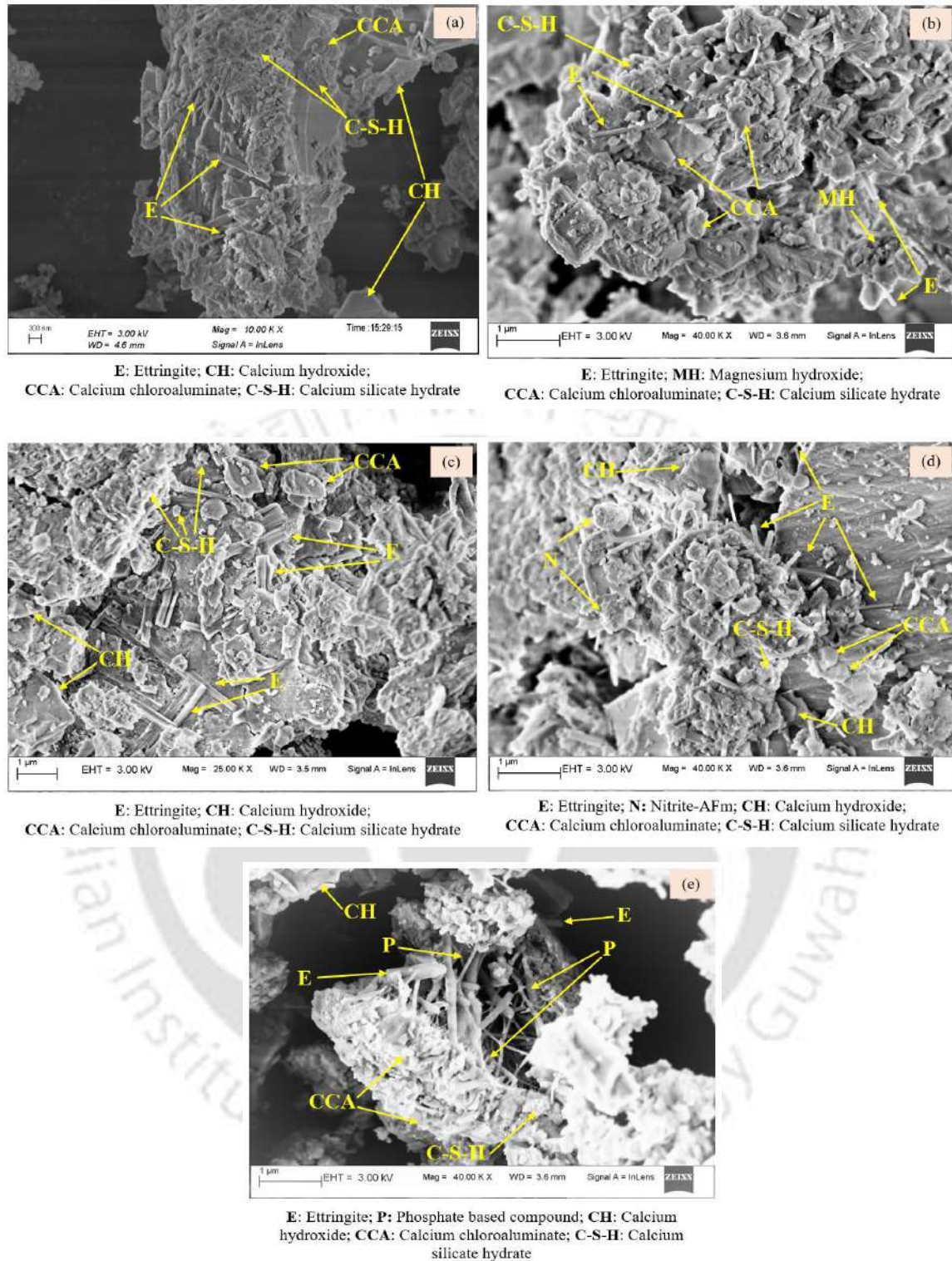


Fig. 6.49 FESEM images of OPC concrete at w/c of 0.55: (a) control mix exposed to 3.5% NaCl solution, (b) control mix exposed to 3.5% MgCl₂ solution, (c) control mix exposed to 3.5% CaCl₂ solution, (d) concrete with 3% NaNO₂, exposed to 3.5% NaCl solution, and (e) concrete with 3% DHP, exposed to 3.5% NaCl solution

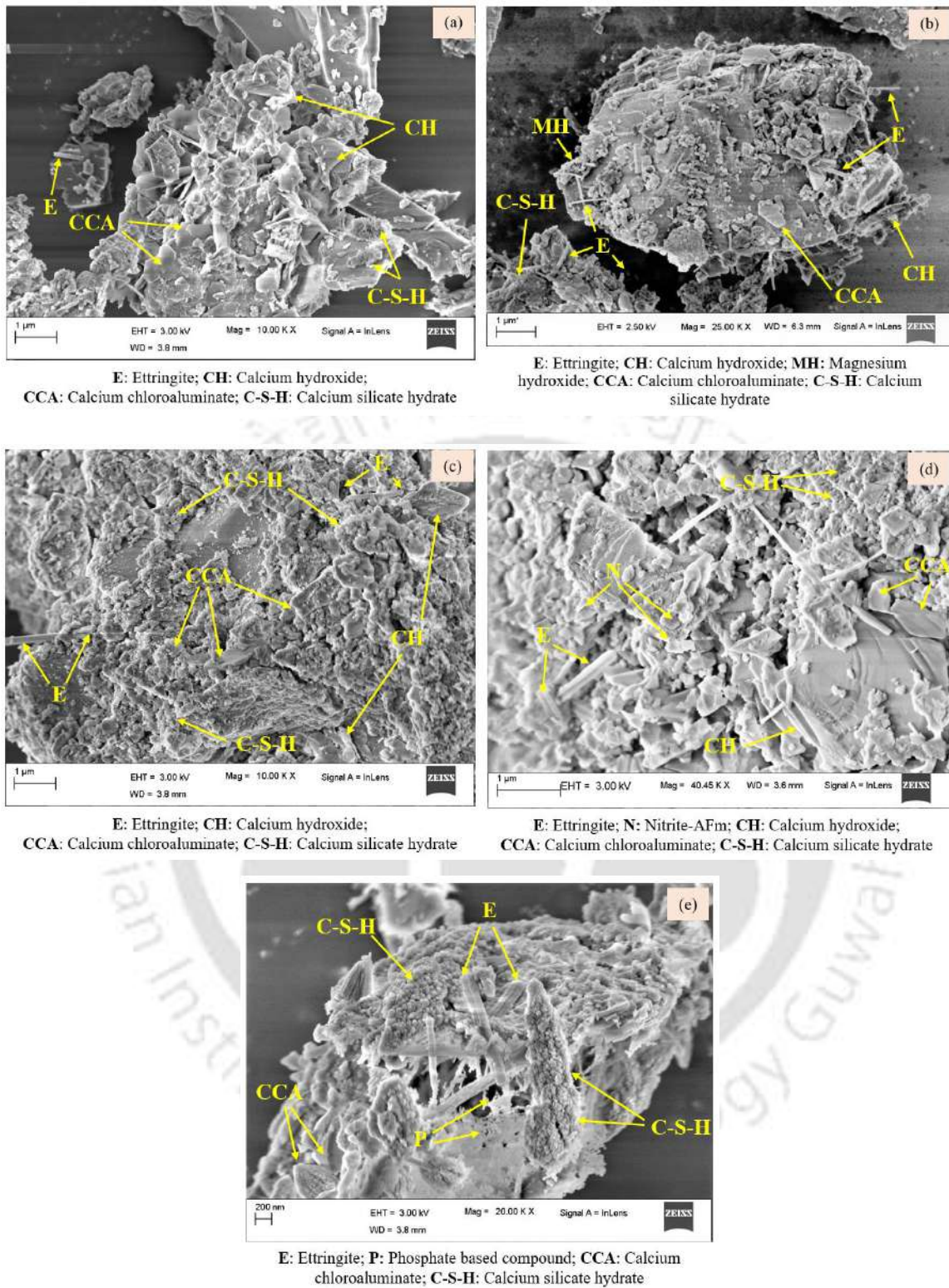


Fig. 6.50 FESEM images of PPC concrete at w/c of 0.55: (a) control mix exposed to 3.5% NaCl solution, (b) control mix exposed to 3.5% MgCl_2 solution, (c) control mix exposed to 3.5% CaCl_2 solution, (d) concrete with 3% NaNO_2 , exposed to 3.5% NaCl solution, and (e) concrete with 3% DHP, exposed to 3.5% NaCl solution

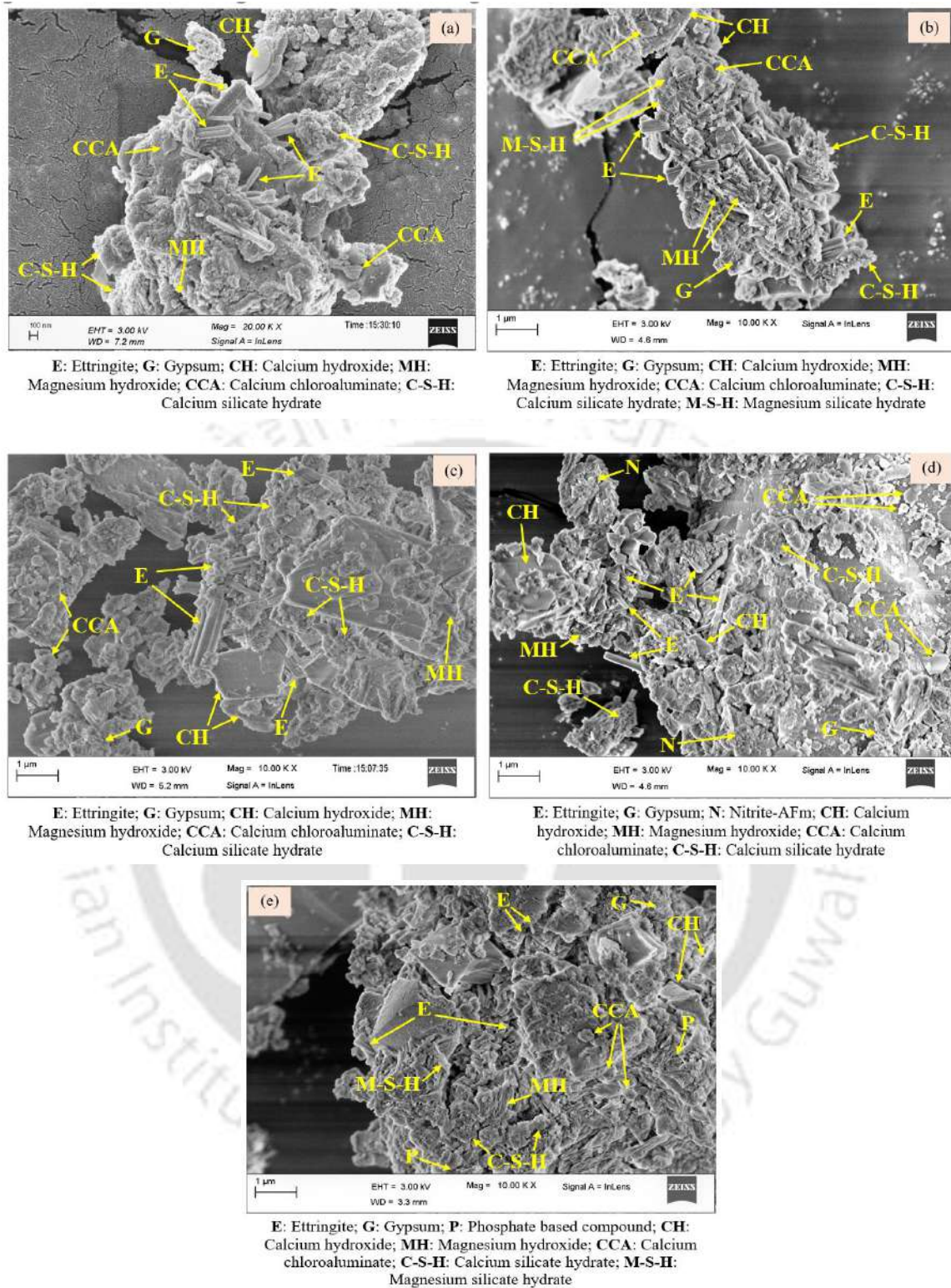


Fig. 6.51 FESEM images of OPC concrete at w/c of 0.45: (a) control mix exposed to 3.5% NaCl+3.5% MgSO₄ solution, (b) control mix exposed to 3.5% MgCl₂+3.5% MgSO₄ solution, (c) control mix exposed to 3.5% CaCl₂+3.5% MgSO₄ solution, (d) concrete with 3% NaNO₂, exposed to 3.5% NaCl+3.5% MgSO₄ solution, and (e) concrete with 3% DHP, exposed to 3.5% NaCl+3.5% MgSO₄ solution

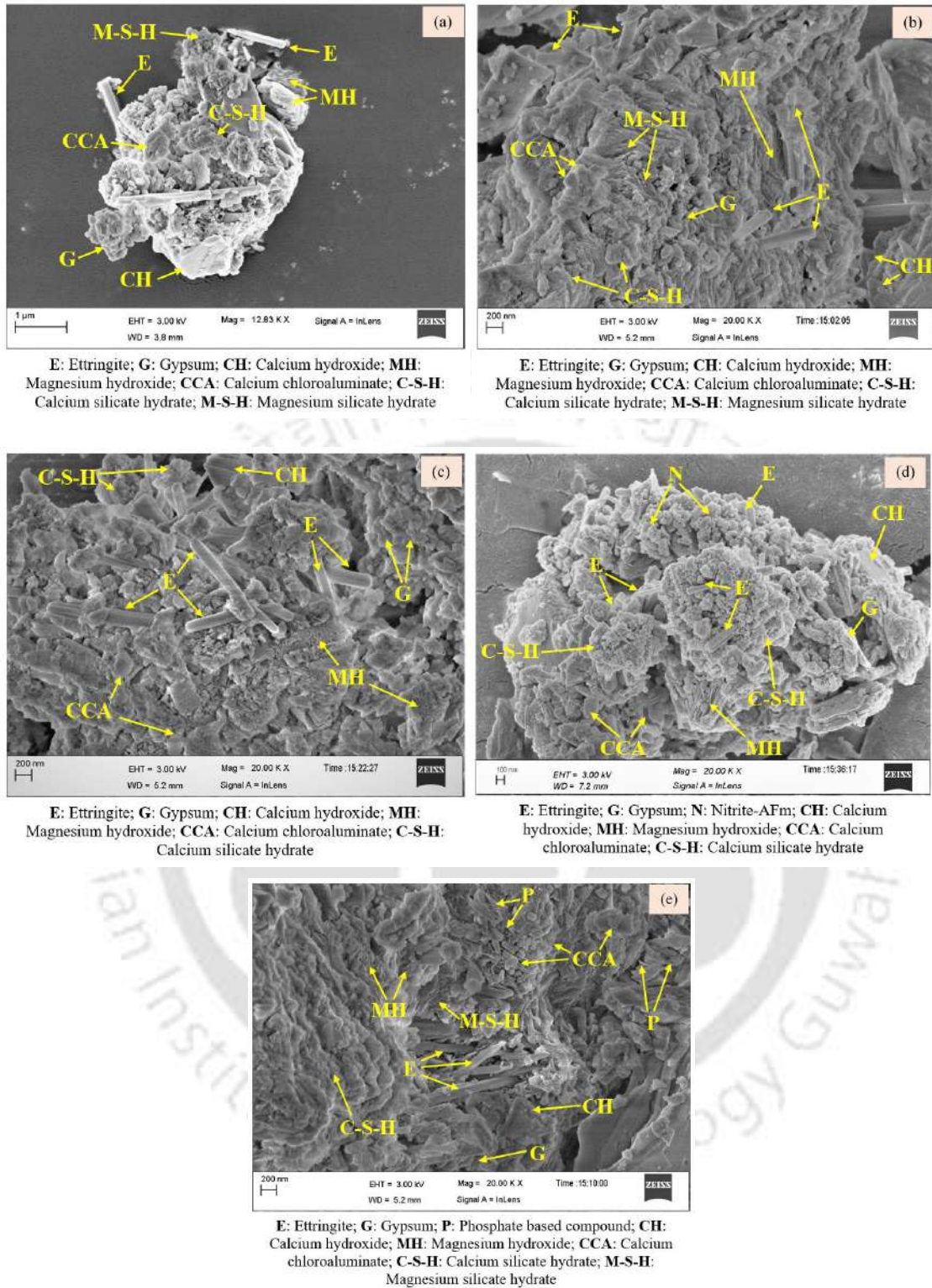


Fig. 6.52 FESEM images of PPC concrete at w/c of 0.45: (a) control mix exposed to 3.5% NaCl+3.5% MgSO₄ solution, (b) control mix exposed to 3.5% MgCl₂+3.5% MgSO₄ solution, (c) control mix exposed to 3.5% CaCl₂+3.5% MgSO₄ solution, (d) concrete with 3% NaNO₂, exposed to 3.5% NaCl+3.5% MgSO₄ solution, and (e) concrete with 3% DHP, exposed to 3.5% NaCl+3.5% MgSO₄ solution

From these figures, it is noted that the morphological form of C-S-H is of cotton-shaped structure [193], and that of calcium hydroxide (portlandite) appeared in large size hexagonal shape crystals. The formation of C-S-H is more in PPC concrete as compared to OPC concrete irrespective of corrosion inhibitors, and exposure solutions as noted from Fig. 6.49 to Fig. 6.52. As stated earlier, this is attributed to the effect of pozzolanic reaction in PPC concrete that results in formation of more C-S-H. The formation of Friedel's salt (CCA) in concrete was observed in the form of small hexagonal slice crystals as evident from Fig. 6.49 to Fig. 6.52. Further, the FESEM images indicated more formation of calcium chloroaluminate in OPC concrete than PPC concrete. The FESEM images shown in Fig. 6.49 to Fig. 6.52 showed the presence of ettringite (E) in concrete mixes in the form of needle shaped crystals, and the formation of ettringite was more in OPC concrete as compared to PPC concrete as evident from the FESEM images. The variations in the formations of calcium chloroaluminate and ettringite between OPC, and PPC concrete as observed from the FESEM images are in line with the weight (%) of these compounds obtained from the XRD analysis. Further, the formation of magnesium hydroxide (MH) in the concrete exposed to $MgCl_2$ solution, and that exposed to composite chloride-sulfate solutions was confirmed by the presence of rosette-like clusters as observed from the FESEM images shown in Fig. 6.49 (b), Fig. 6.50 (b), Fig. 6.51, and Fig. 6.52. In addition, the FESEM images (Fig. 6.51, and Fig. 6.52) showed fibrous magnesium silicate hydrate (M-S-H), and gypsum (G) crystals in the shape of layers of ice like plate in the concrete mixes exposed to composite chloride-sulfate solutions. From Fig. 6.49 (d), Fig. 6.50 (d), Fig. 6.51 (d), and Fig. 6.52 (d), the presence of nitrite-AFm in the concrete admixed with $NaNO_2$ was observed in the form of petal shaped crystals [132]. Further, rod-shaped morphology of phosphate based compounds was observed in the FESEM images (Fig. 6.49 (e), Fig. 6.50 (e), Fig. 6.51 (e), and Fig. 6.52 (e)) of concrete admixed with DHP [25].

6.5 Summary

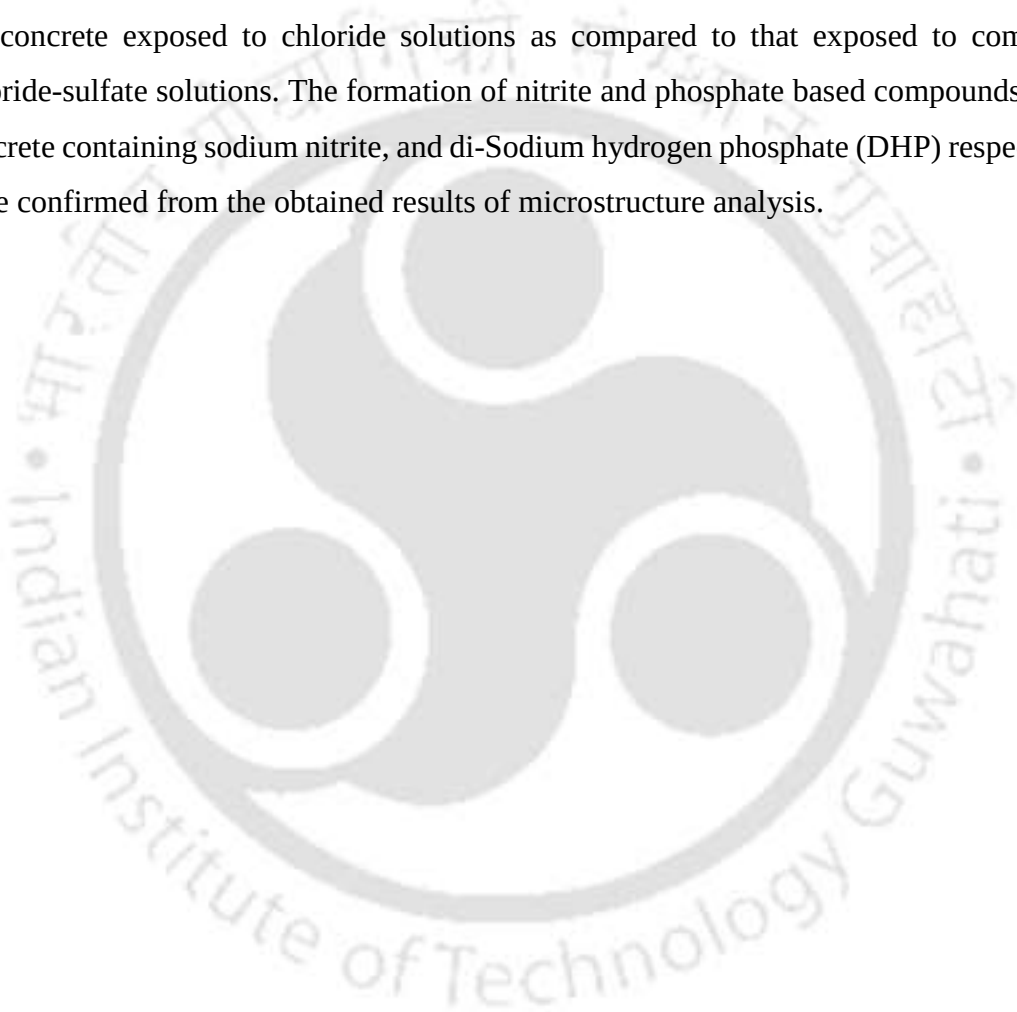
The results obtained from half-cell potential, and linear polarization measurements on cylindrical reinforced concrete specimens subjected to different chloride solutions indicated that NaCl is more aggressive in depassivating the reinforcing steel early thereby reducing the corrosion initiation period, and also increasing the corrosion current density as compared to $CaCl_2$ solution followed by $MgCl_2$ solution for control concrete as well as that admixed with corrosion inhibitors for both OPC, and PPC. However, in case of exposure to composite chloride-sulfate solutions, concrete specimens subjected to

CaCl₂+MgSO₄ solution mostly showed more negative half-cell potential, and higher corrosion current density as compared to NaCl+MgSO₄ followed by MgCl₂+MgSO₄ solutions for both OPC, and PPC concrete admixed with, and without corrosion inhibitors over the entire exposure period. Addition of corrosion inhibitors, i.e., sodium nitrite, and di-Sodium hydrogen phosphate (DHP) enhanced the resistance of concrete against corrosion of steel reinforcement in case of exposure to chloride, and composite chloride-sulfate solutions for both cements. In case of OPC concrete, the specimens exposed to chloride solutions mostly showed more negative half-cell potential (E_0), and higher corrosion current density (I_{corr}) as compared to that exposed to composite chloride-sulfate solutions. However, in case of PPC concrete, there was no systematic variation in E_0 , and I_{corr} between chloride, and composite chloride-sulfate solutions.

In case of exposure to chloride solutions, the concrete containing NaNO₂ showed more negative E_0 , and higher I_{corr} during the early exposure period as compared to DHP whereas the opposite variation was observed during the later exposure period where the difference in I_{corr} between NaNO₂, and DHP was more substantial. This indicates that NaNO₂ exhibited improved resistance against chloride induced corrosion of steel reinforcement than DHP even in the presence of higher amount of chloride ions near steel reinforcement. At higher dosage of corrosion inhibitors, the efficacy of both the inhibitors against corrosion increased as the E_0 became less negative as well as the I_{corr} decreased with increase in the dosage of inhibitors. Both corrosion inhibitors were comparatively more effective against corrosion of steel reinforcement in OPC concrete than PPC concrete. In PPC concrete, the formation of denser microstructure was more dominant in minimizing the extent of corrosion over the effect of corrosion inhibitors as the formation denser microstructure decreased the ingress of chloride ions thereby resulting in significantly lower I_{corr} in PPC concrete than OPC concrete.

For both chloride, and composite chloride-sulfate solutions, addition of corrosion inhibitors in concrete decreased the free chloride ion content near rebar level as compared to control concrete irrespective of cement type, and exposure solution whereas the opposite variation was observed in case of bound chloride ion content. In case of exposure to only chloride solutions, the free chloride ion content near rebar level was higher in the concrete containing NaNO₂ whereas the bound chloride ion content was higher in the concrete containing DHP. However, in case of concrete exposed to composite chloride-sulfate solutions, there was no systematic variation in free chloride content, and bound chloride

content between the corrosion inhibitors. From the obtained results of microstructure analysis (XRD, FTIR and FESEM analyses), the variations in the formation of different compounds in concrete were analyzed with cement type, w/c, and corrosion inhibitor in case of exposure to chloride, and composite chloride-sulfate solutions. The XRD analysis showed mostly more formation of calcium hydroxide, calcium chloroaluminate, and ettringite in OPC concrete than PPC concrete irrespective of addition of corrosion inhibitors, and exposure solutions, i.e., chloride, and composite chloride-sulfate solutions. Further, the results of XRD analysis showed more amount of calcium chloroaluminate in the concrete exposed to chloride solutions as compared to that exposed to composite chloride-sulfate solutions. The formation of nitrite and phosphate based compounds in the concrete containing sodium nitrite, and di-Sodium hydrogen phosphate (DHP) respectively were confirmed from the obtained results of microstructure analysis.



Chloride Ingress, and Chloride Binding in Concrete Admixed with Corrosion Inhibitors and Exposed to Chloride and Composite Chloride-Sulfate Environment

7.1 General

In this chapter, the results of compressive strength of concrete prepared from OPC and PPC at water-to-cement ratios (w/c) of 0.45 and 0.55, and admixed with or without corrosion inhibitors are presented and discussed. The results of free chloride ion (C_F) and total chloride ion (C_T) contents of concrete from varying depth intervals of cube specimens exposed to chloride and composite chloride-sulfate solutions, at the end of exposure period, i.e., 756 days of exposure are discussed. From the experimentally obtained chloride content values, the apparent chloride diffusion coefficient (D_{app}) and chloride binding capacity (R) of concrete were calculated and the obtained results are discussed in this chapter. Further, in this chapter, the effects of different parameters such as depth from the exposure surface of concrete, cement type, w/c, exposure solutions (i.e., chloride and composite chloride-sulfate solutions), and corrosion inhibitors on variations in free chloride content, apparent chloride diffusion coefficient and chloride binding capacity of concrete are evaluated and discussed. Besides, the effects of above parameters on microstructure of concrete were studied by XRD analysis, FESEM analysis and FTIR analysis, and the obtained results are presented and discussed in this chapter.

7.2 Compressive strength of concrete

The results of 28-day compressive strength test carried out on OPC and PPC control cube specimens (without corrosion inhibitors) and those containing corrosion inhibitors at 3% concentration are shown in Table 7.1. Each value of compressive strength shown in this table represents the average value obtained from the results of three replicate cube specimens of a given concrete mix. In addition, the standard deviation values were also calculated for compressive strength of each concrete mix and are presented in Table 7.1. It may be noted that the compressive strength of concrete made with w/c of 0.45 and admixed with corrosion inhibitors at 3% concentration are already presented (Table 4.1) and discussed in Chapter 4. These results are presented here again in Table 7.1 to compare with that of concrete made with w/c of 0.55.

Table 7.1 28-day average compressive strength along with standard deviation of concrete mixes

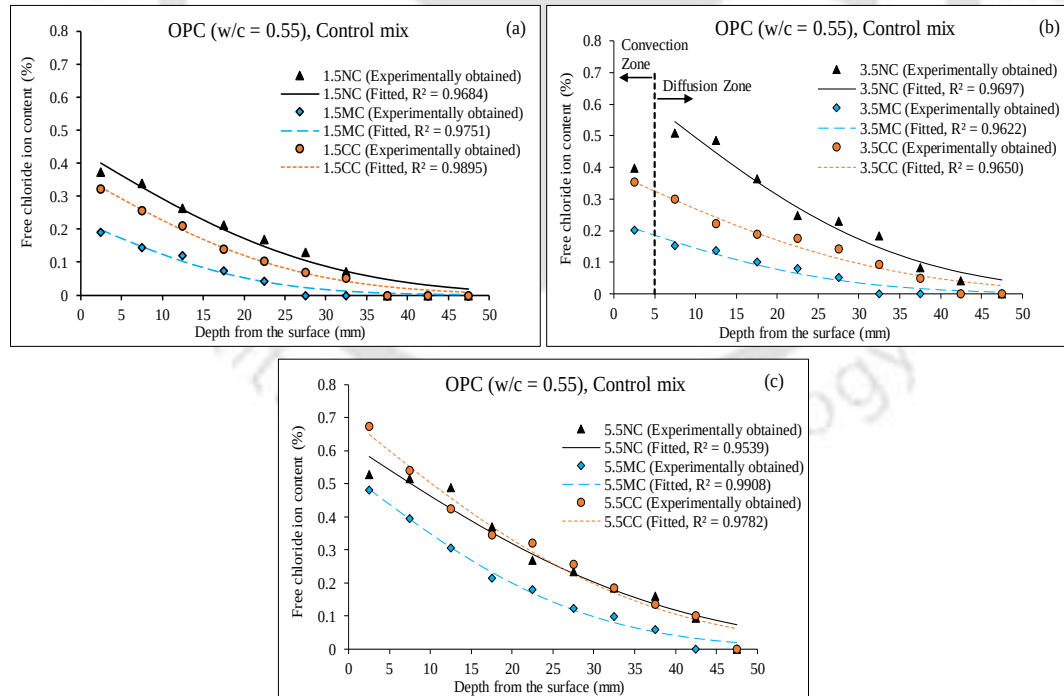
Water-to-cement ratio (w/c)	Cement type	Admixed corrosion inhibitor concentration (% by weight of cement)	Compressive strength (N/mm ²)	Standard deviation (N/mm ²)
0.45	OPC	0% (Control)	42.81	0.55
		3% NaNO ₂	36.60	0.91
		3% DHP	28.30	1.46
	PPC	0% (Control)	37.04	0.55
		3% NaNO ₂	36.44	1.30
		3% DHP	24.00	0.36
0.55	OPC	0% (Control)	32.44	0.73
		3% NaNO ₂	29.93	1.27
		3% DHP	26.37	0.20
	PPC	0% (Control)	30.22	1.45
		3% NaNO ₂	29.33	0.63
		3% DHP	19.40	0.42

From Table 7.1, it is inferred that the addition of sodium nitrite (NaNO₂) and di-Sodium hydrogen phosphate (DHP) lowered the compressive strength of concrete mixes when compared with control concrete for both types of cement and w/c, with higher reduction in compressive strength in case of DHP. As already discussed in Chapter 4, the retarding effect of NaNO₂ on strength development may be responsible for the reduced compressive strength of the specimens containing NaNO₂. The cause of reduction in compressive strength of concrete containing DHP may be due to the effect of reaction between phosphates and cement compounds, which led to the production of water and phosphate compounds namely acidic hydrated pyrophosphate (Ca₃H₂(P₂O₇)₂.H₂O) and dicalcium phosphate dihydrate (brushite: CaHPO₄.2H₂O) [131]. These lead to disappearance of cement hydration products, which are essential for the strength development process of concrete. In addition, the precipitation of calcium phosphate due to reaction of phosphate and calcium hydroxide delays the setting time of cement, which might have resulted in lower strength development in the concrete admixed with DHP [83]. Between the corrosion inhibitors, the concrete containing NaNO₂ showed higher compressive than that containing DHP and the percentage increase in compressive strength was 17.29% for OPC, and 33.98% for PPC irrespective of w/c. The order of decrease in 28-day compressive strength of control mix, and those containing corrosion inhibitors is found to be: control concrete > concrete containing NaNO₂ > concrete containing DHP. While comparing the effect of cement type, it is noted that for both control concrete, and the concrete containing corrosion

inhibitors, OPC exhibited higher compressive strength than PPC. This can be ascribed to the dominant effect of hydration reaction in OPC concrete over the effect of pozzolanic reaction in PPC concrete in the development of early age compressive strength [163, 164]. From Table 7.1, it is observed that the compressive strength of control concrete as well as those admixed with corrosion inhibitors decreased with increase in w/c regardless of the type of cement, and corrosion inhibitor.

7.3 Free chloride ion content and apparent chloride diffusion coefficient of concrete

As stated in Chapter 3, the concrete powder samples collected at different depth intervals from the exposure surface of cube specimens were used for determining the free chloride ion (C_F) content and total chloride ion (C_T) content of concrete exposed to different chloride and composite chloride-sulfate solutions. Typical profiles of experimentally obtained free chloride ion (C_F) content and the corresponding fitted chloride profiles of concrete powder samples obtained from OPC and PPC concrete mixes admixed with or without corrosion inhibitors at w/c of 0.45 and 0.55, and exposed to varying concentrations (i.e., 1.5%, 3.5%, and 5.5%) of NaCl, MgCl₂, and CaCl₂ solutions for a period 756 days are shown in Fig. 7.1 to Fig. 7.6. The remaining plots are presented in Appendix B: Fig. B1 to Fig. B6.



NC: Sodium chloride; MC: Magnesium chloride; CC: Calcium chloride

Fig. 7.1 Experimentally obtained and fitted free chloride ion (C_F) content profile of control concrete made from OPC at w/c of 0.55 and exposed to chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂) of different concentrations: (a) 1.5%, (b) 3.5%, and (c) 5.5%

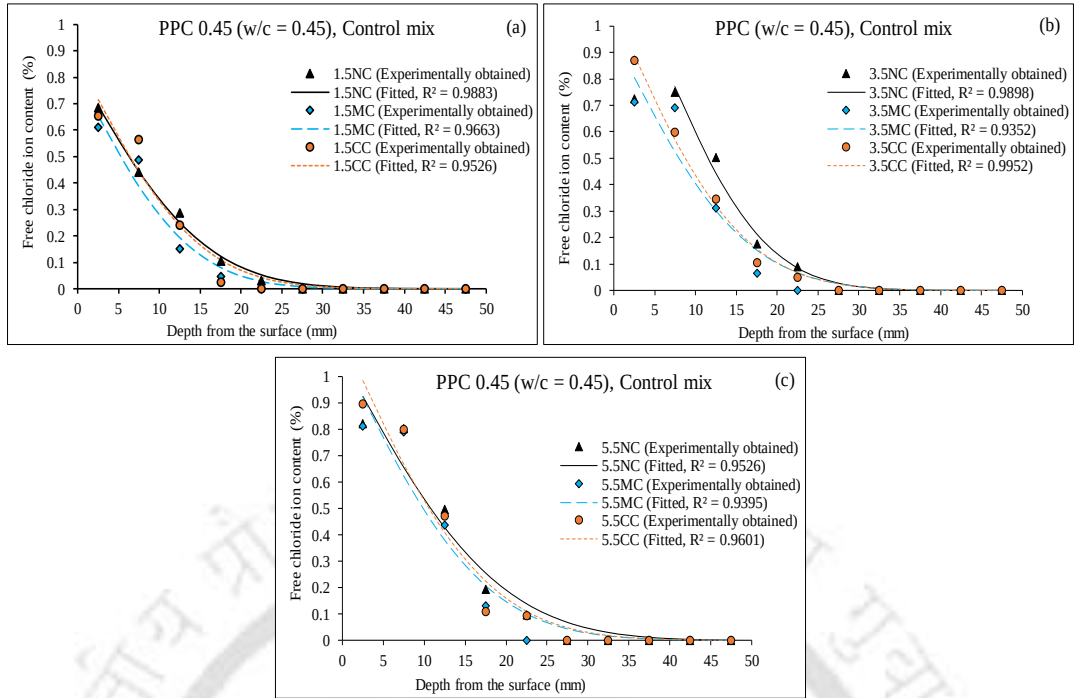
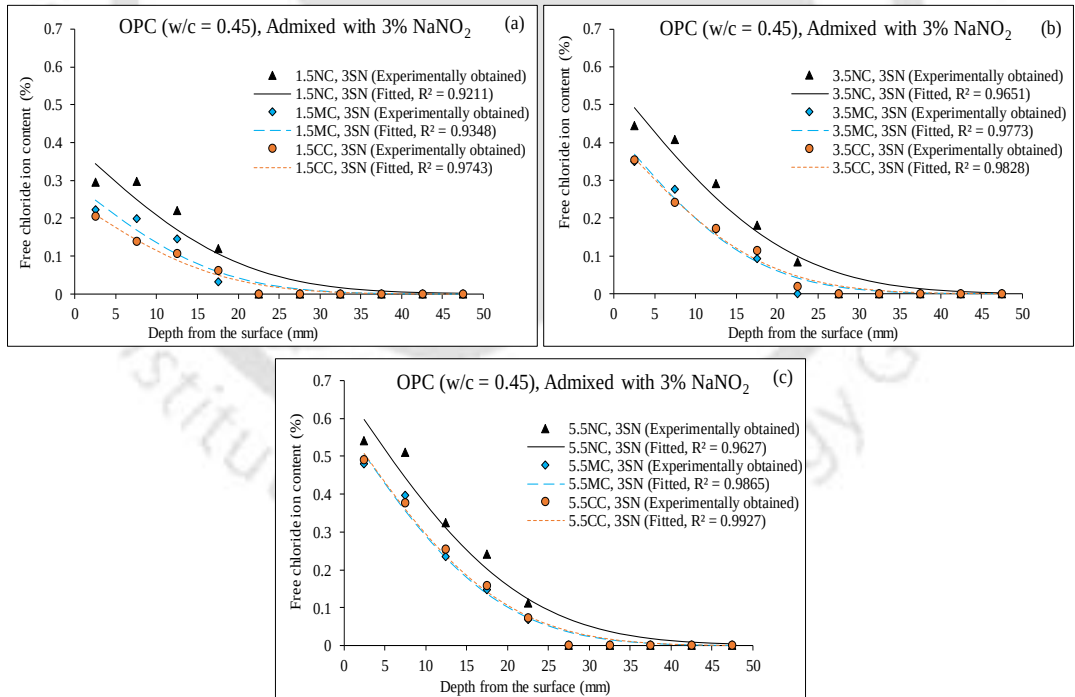


Fig. 7.2 Experimentally obtained and fitted free chloride ion (C_F) content profile of control concrete made from PPC at w/c of 0.45 and exposed to chloride salt solutions (i.e., NaCl, $MgCl_2$, and $CaCl_2$) of different concentrations: (a) 1.5%, (b) 3.5%, and (c) 5.5%



SN: Sodium nitrite

Fig. 7.3 Experimentally obtained and fitted free chloride ion (C_F) content profile of OPC concrete containing 3% $NaNO_2$ at w/c of 0.45 and exposed to chloride salt solutions (i.e., NaCl, $MgCl_2$, and $CaCl_2$) of different concentrations: (a) 1.5%, (b) 3.5%, and (c) 5.5%

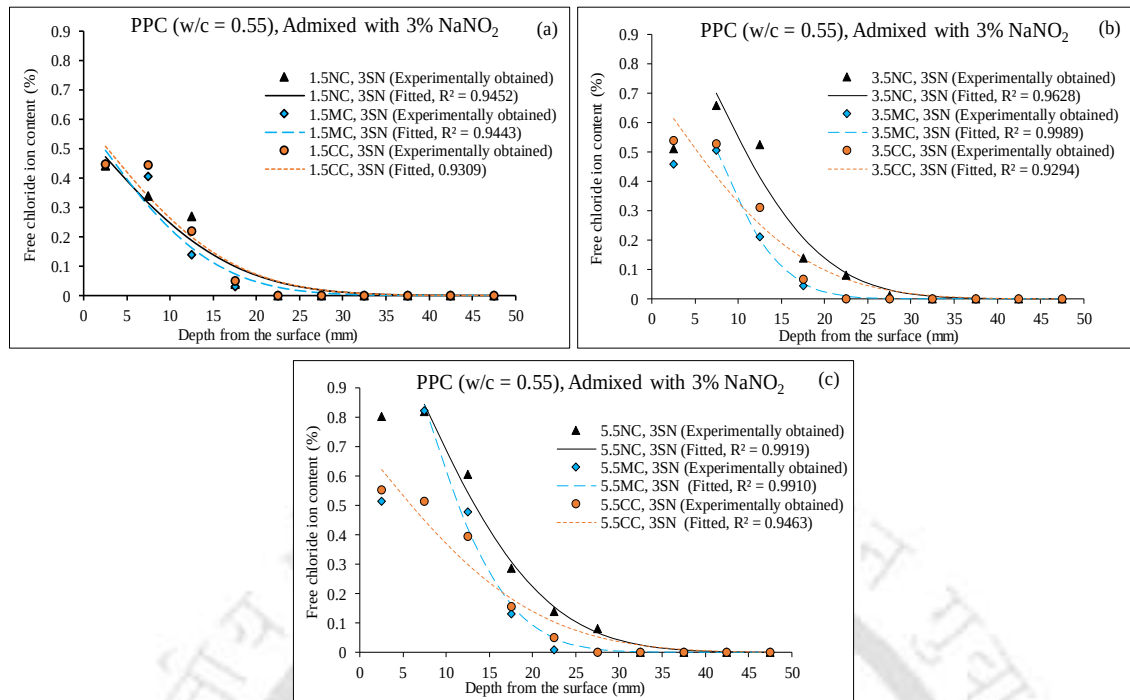
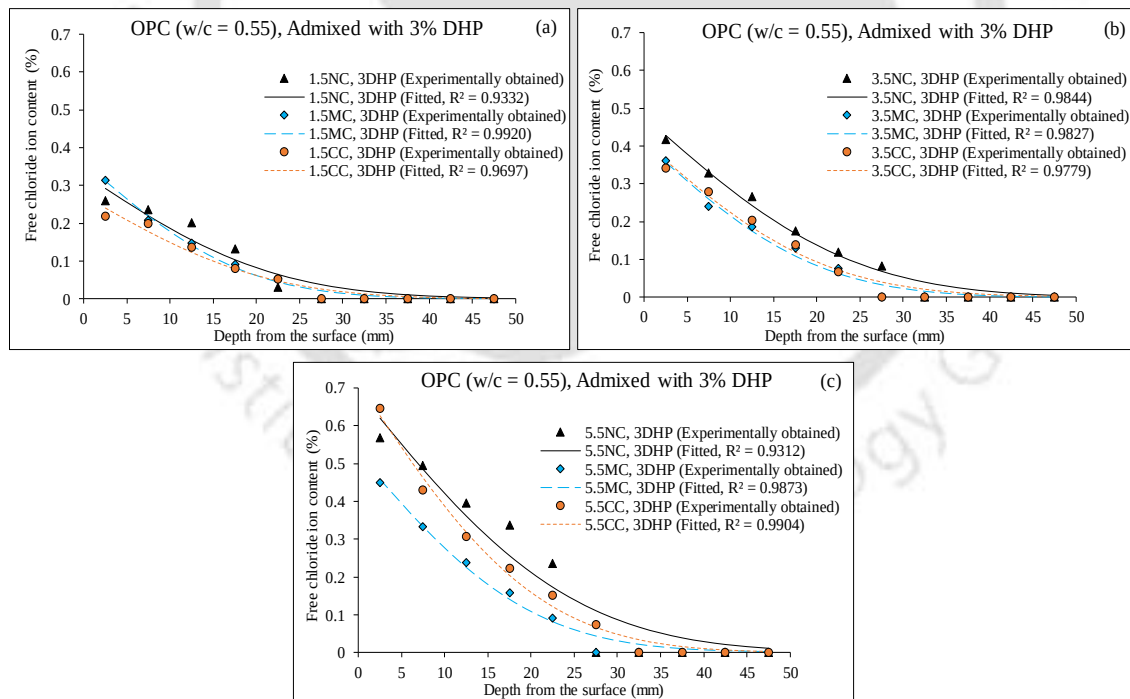


Fig. 7.4 Experimentally obtained and fitted free chloride ion (C_F) content profile of PPC concrete containing 3% NaNO₂ at w/c of 0.55 and exposed to chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂) of different concentrations: (a) 1.5%, (b) 3.5%, and (c) 5.5%



DHP: di-Sodium hydrogen phosphate

Fig. 7.5 Experimentally obtained and fitted free chloride ion (C_F) content profile of OPC concrete containing 3% DHP at w/c of 0.55 and exposed to chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂) of different concentrations: (a) 1.5%, (b) 3.5%, and (c) 5.5%

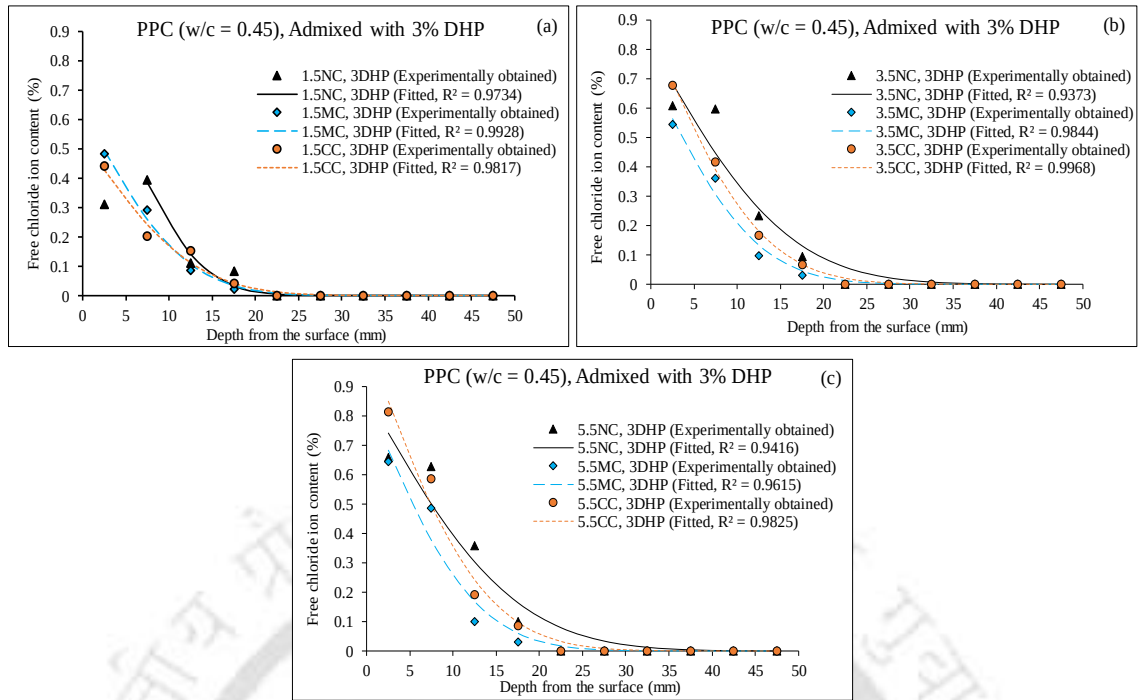
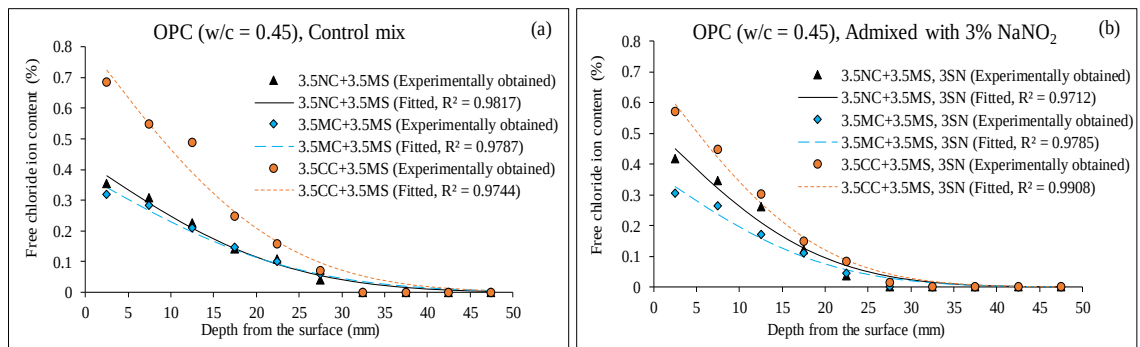


Fig. 7.6 Experimentally obtained and fitted free chloride ion (C_F) content profile of PPC concrete containing 3% DHP at w/c of 0.45 and exposed to chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂) of different concentrations: (a) 1.5%, (b) 3.5%, and (c) 5.5%

The plots of experimentally obtained free chloride ion (C_F) content and the corresponding fitted chloride profiles of concrete powder samples collected from OPC and PPC concrete mixes admixed with or without corrosion inhibitors at w/c of 0.45 and 0.55, and exposed to composite chloride-sulfate solutions (i.e., 3.5% NaCl+3.5% MgSO₄, 3.5% MgCl₂+3.5% MgSO₄, and 3.5% CaCl₂+3.5% MgSO₄) for a period 756 days are shown in Fig. 7.7 to Fig. 7.10.



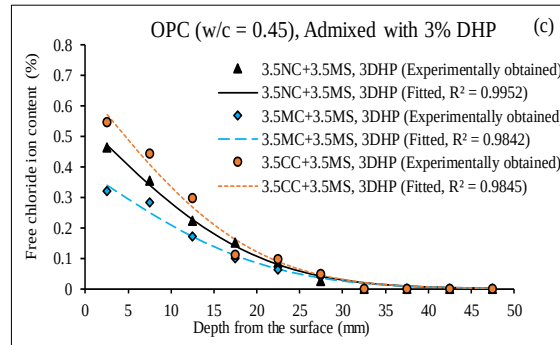


Fig. 7.7 Experimentally obtained and fitted free chloride ion (C_F) content profile of OPC concrete at w/c of 0.45 and exposed to composite chloride-sulfate solutions: (a) control mix, (b) concrete containing 3% NaNO_2 , and (c) concrete containing 3% DHP

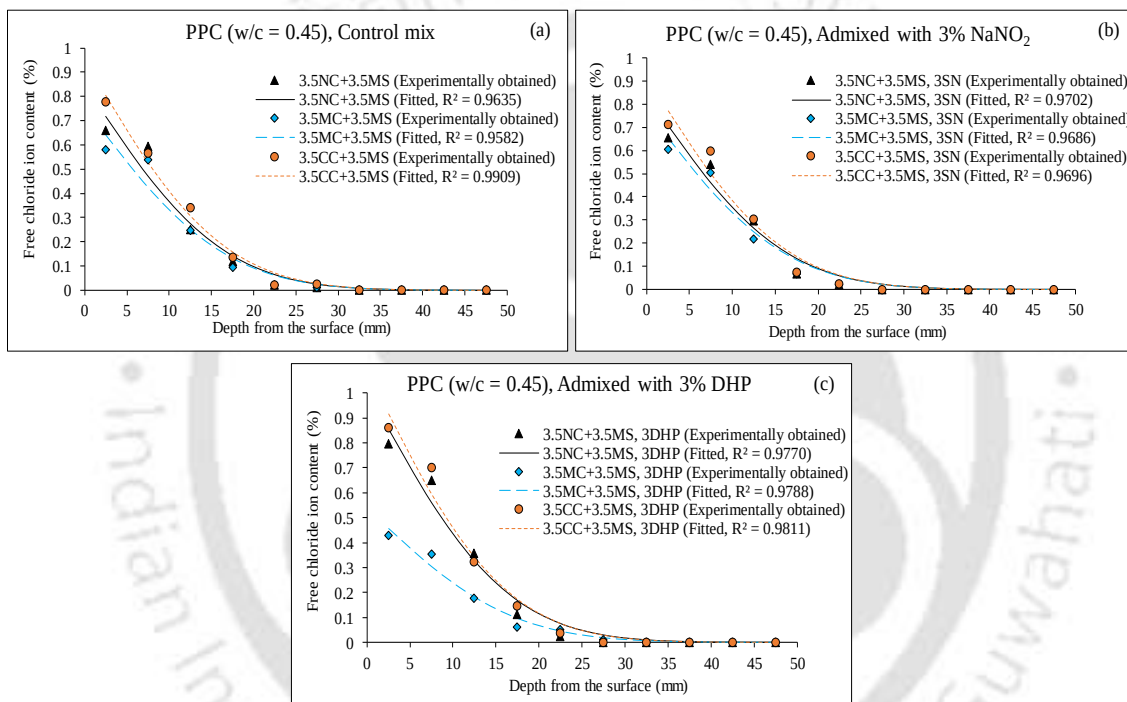
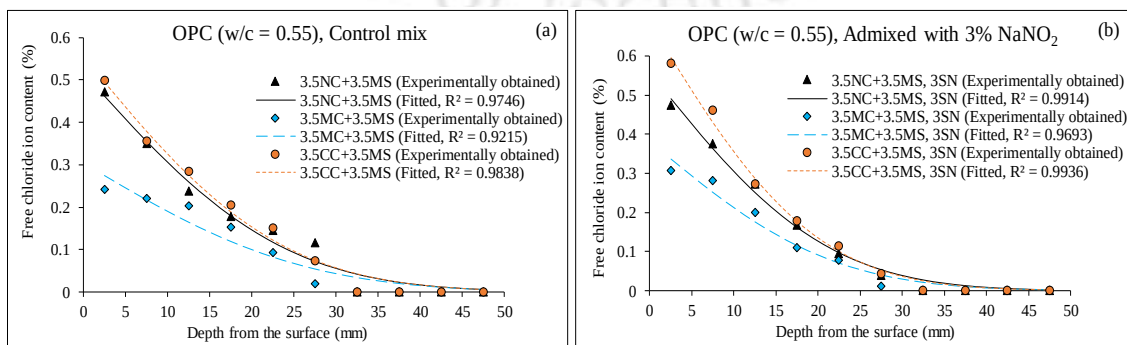


Fig. 7.8 Experimentally obtained and fitted free chloride ion (C_F) content profile of PPC concrete at w/c of 0.45 and exposed to composite chloride-sulfate solutions: (a) control mix, (b) concrete containing 3% NaNO_2 , and (c) concrete containing 3% DHP



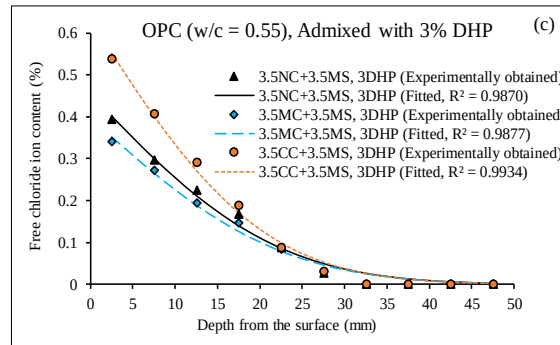


Fig. 7.9 Experimentally obtained and fitted free chloride ion (C_F) content profile of OPC concrete at w/c of 0.55 and exposed to composite chloride-sulfate solutions: (a) control mix, (b) concrete containing 3% NaNO_2 , and (c) concrete containing 3% DHP

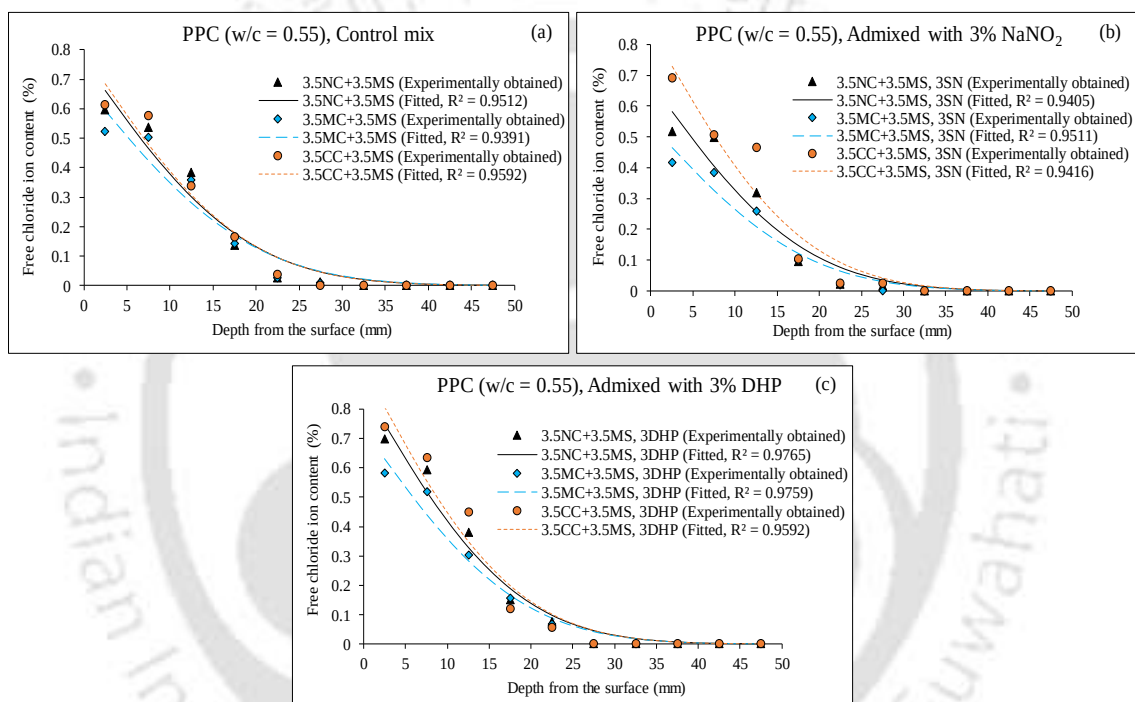


Fig. 7.10 Experimentally obtained and fitted free chloride ion (C_F) content profile of PPC concrete at w/c of 0.55 and exposed to composite chloride-sulfate solutions: (a) control mix, (b) concrete containing 3% NaNO_2 , and (c) concrete containing 3% DHP

As stated earlier in Chapter 3, the apparent chloride diffusion coefficient (D_{app}) of OPC and PPC concrete mixes were calculated by fitting the best-fit relationship of the analytical solution of Fick's second law of diffusion to the experimentally obtained free chloride ion (C_F) content at various depth intervals from the exposure surface of concrete. The obtained values of D_{app} are shown in Fig. 7.11 to Fig. 7.14 for concrete exposed to chloride solutions, and in Fig. 7.15 and Fig. 7.16 for concrete exposed to composite chloride-sulfate solutions. In some cases, the convection zone was observed in the depth interval of 0-5 mm from the exposure surface of concrete specimens. In those cases, the free chloride ion content in the

convection zone was excluded from the free chloride ion content profile for estimating the apparent chloride diffusion coefficient (D_{app}) of concrete.

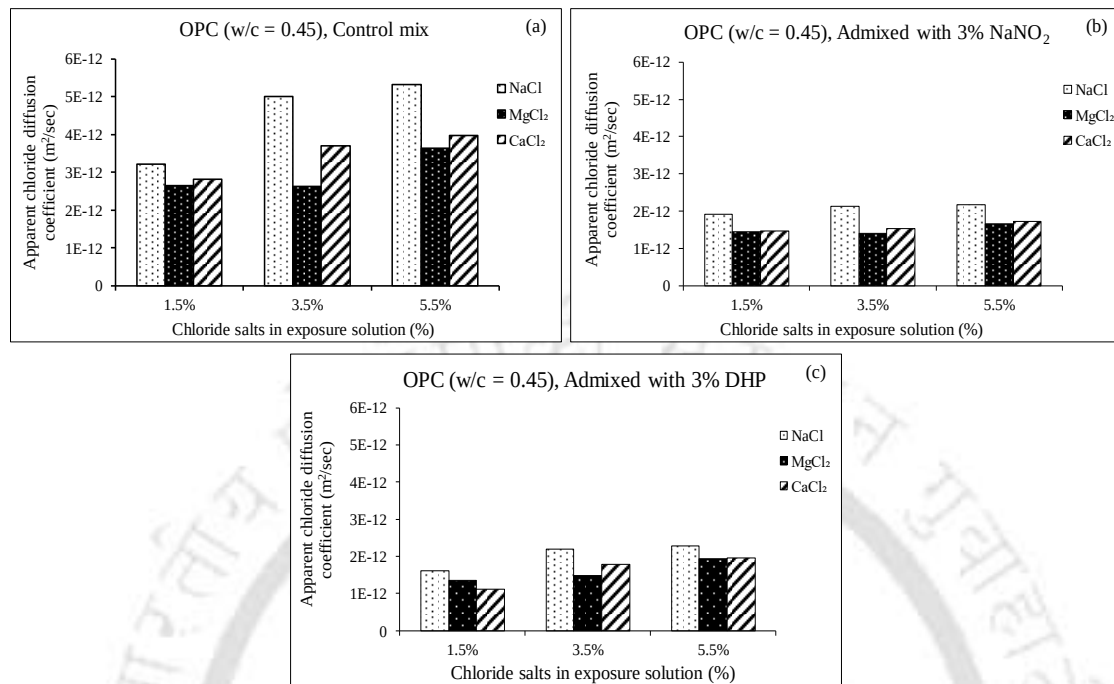


Fig. 7.11 Apparent chloride diffusion coefficient of OPC concrete at w/c of 0.45 and exposed to different chloride salt solutions: (a) control mix, (b) concrete admixed with 3% $NaNO_2$, and (c) concrete admixed with 3% DHP

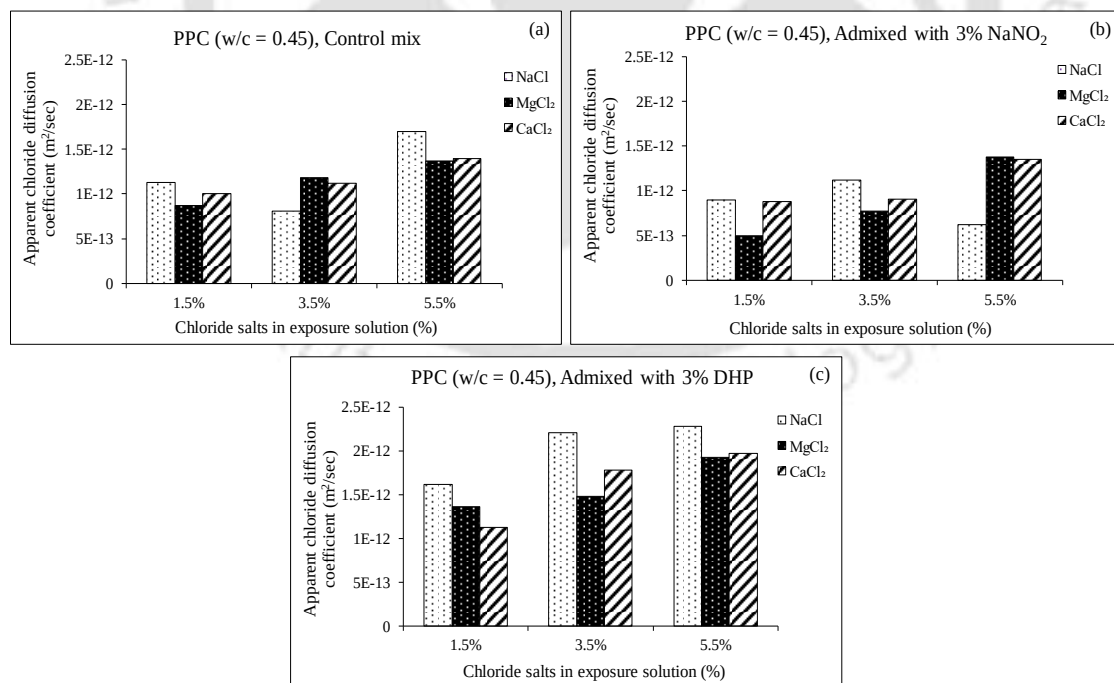


Fig. 7.12 Apparent chloride diffusion coefficient of PPC concrete at w/c of 0.45 and exposed to different chloride salt solutions: (a) control mix, (b) concrete admixed with 3% $NaNO_2$, and (c) concrete admixed with 3% DHP

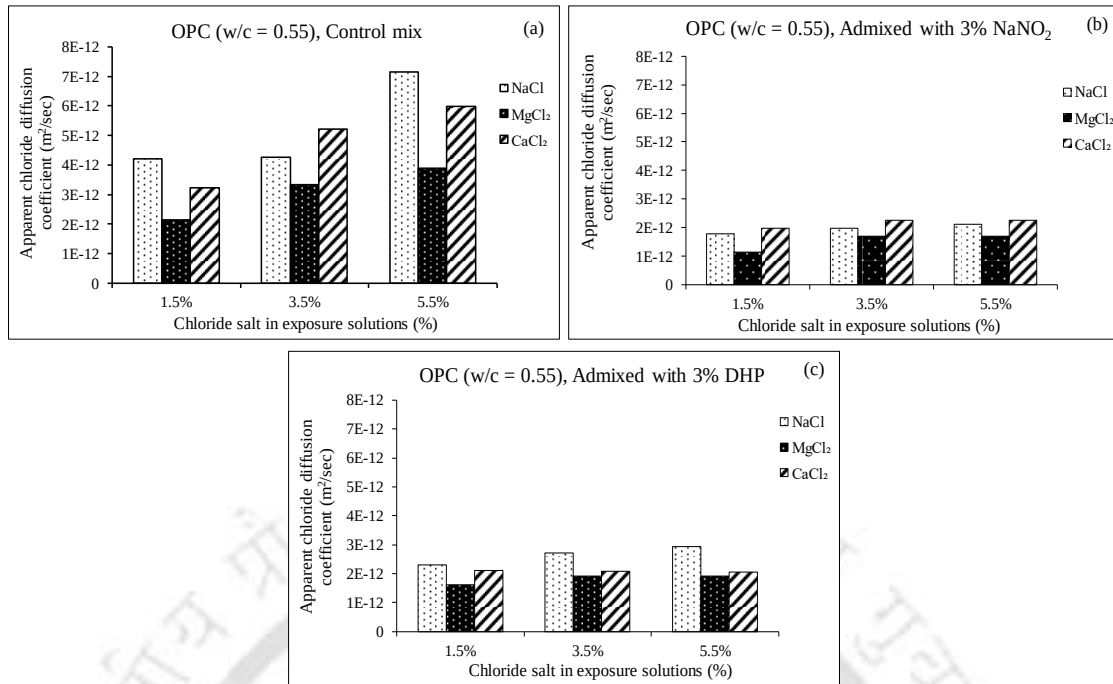


Fig. 7.13 Apparent chloride diffusion coefficient of OPC concrete at w/c of 0.55 and exposed to different chloride salt solutions: (a) control mix, (b) concrete admixed with 3% NaNO_2 , and (c) concrete admixed with 3% DHP

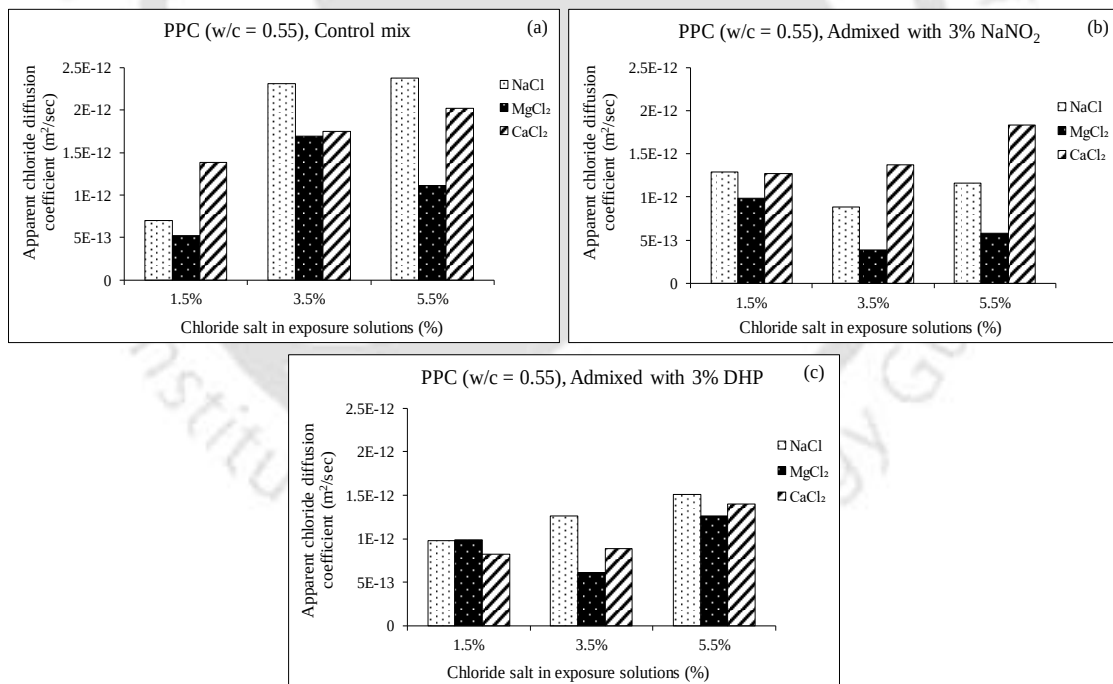


Fig. 7.14 Apparent chloride diffusion coefficient of PPC concrete at w/c of 0.55 and exposed to different chloride salt solutions: (a) control mix, (b) concrete admixed with 3% NaNO_2 , and (c) concrete admixed with 3% DHP

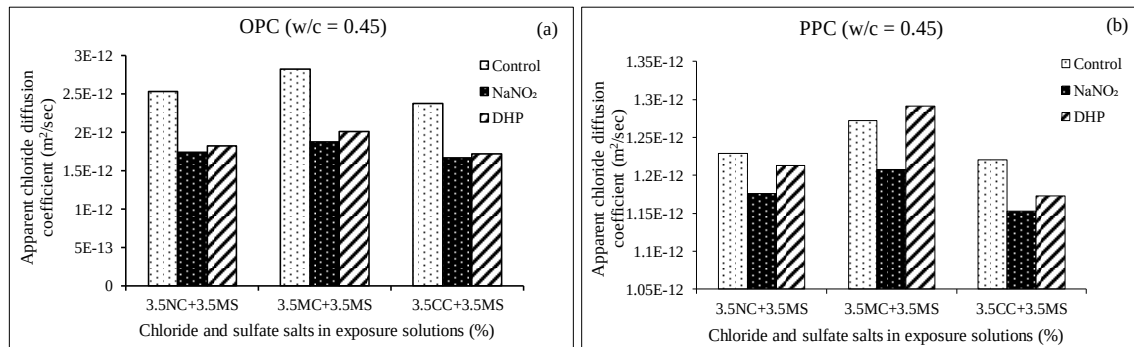


Fig. 7.15 Apparent chloride diffusion coefficient of concrete at w/c of 0.45 and exposed to different composite chloride-sulfate solutions: (a) OPC, and (b) PPC

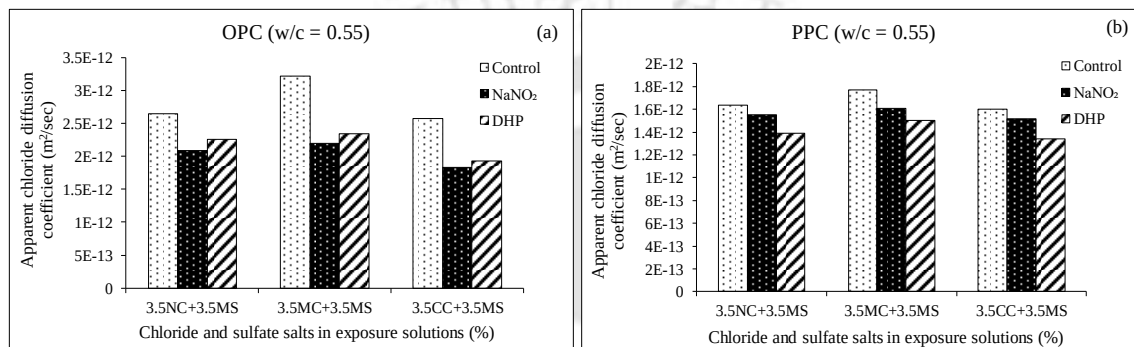


Fig. 7.16 Apparent chloride diffusion coefficient of concrete at w/c of 0.55 and exposed to different composite chloride-sulfate solutions: (a) OPC, and (b) PPC

7.3.1 Effect of depth from exposure surface of concrete on free chloride profile

From Fig. 7.1 to Fig. 7.10, and Appendix B: Fig. B1 to Fig. B6, it is observed that the free chloride ion (C_F) content in concrete exposed to chloride and composite chloride-sulfate solutions decreased with increase in depth from the exposure surface thereby indicating lower amount of chloride ingress in concrete at higher depth intervals from the exposure surface. This behavior of chloride transport in concrete is mainly attributed to the effect of capillary suction, and chloride diffusion in concrete [50]. However, in few cases where the concrete specimens were exposed to $NaCl$ and $MgCl_2$ solutions, the free chloride ion content in the depth interval of 0-5 mm was less than that in the adjacent depth interval, i.e., 5-10 mm from the exposure surface of concrete. This may be attributed to the effect of presence of convection zone (shown in Fig. 7.1 (b)) near the surface region of concrete exposed to alternating wetting-drying cycles. The chloride transport in the interior portion of concrete is dominated by diffusion process (due to concentration gradient) while in the surface region of concrete, both convection (due to capillary suction), and diffusion mechanisms exist [50, 157-159]. The formation of convection zone was more in the concrete prepared from PPC as compared to that prepared from OPC [194], which may be

attributed to the effect of variation in leaching of calcium hydroxide in the presence of chloride ions, and the effect of lower degree of pozzolanic reaction near the surface zone in PPC concrete that might have affected the pore structure of PPC concrete to a higher degree as compared to OPC concrete. Between the w/c, the formation of convection zone was more in the concrete prepared at w/c of 0.55 than that prepared at w/c of 0.45 irrespective of cement type, presence and type of corrosion inhibitors, and cation type of chloride salts (i.e., NaCl and MgCl₂) in the exposure solution as evident from Fig. 7.1 to Fig. 7.6 and Appendix B: Fig. B1 to Fig. B6. This may be attributed to the effect of alteration in the capillary suction through the pore network of concrete near the surface zone to a comparatively higher extent in the concrete made with w/c of 0.55. While comparing the effect of cation type of chloride salt, it is observed that the formation of convection zone was more in the concrete exposed to NaCl solution as compared to that exposed to MgCl₂ solution irrespective of cement type, w/c, and presence and type of corrosion inhibitors. This may be due to the effect of leaching of calcium ions from the surface zone of concrete in the presence of NaCl to a higher extent thereby altering the pore structure of concrete near the surface zone as compared to that in the concrete exposed to MgCl₂ solution. Between the corrosion inhibitors, the formation of convection zone was more in the concrete admixed with NaNO₂ as compared to that admixed with DHP irrespective of cement type, w/c, and cation type of chloride salts (i.e., NaCl and MgCl₂) in the exposure solution. This may be ascribed to the effect of presence of negatively charged nitrite ions (NO₂⁻ ions) in the concrete admixed with NaNO₂ that might have repelled the negatively charged chloride ions to a comparatively higher extent in the depth interval of 0-5 mm. Besides, in the concrete admixed with DHP, the reaction of phosphate ions with chloride and Ca²⁺ ions forms chlorapatite (Ca₅(PO₄)₃Cl) [189] that leads to binding of chloride ions thereby reducing free chloride ion content, and resulting in leaching of calcium ions from the surface zone of concrete to a lower extent. The presence of convection zone was not observed in the concrete specimens exposed to composite chloride-sulfate solutions irrespective of cement type, w/c, presence and type of corrosion inhibitors, and cation type of chloride salt in the composite chloride-sulfate solutions as evident from Fig. 7.7 to Fig. 7.10. This may be attributed to the fact that the presence of sulfate ions might have affected the leaching of calcium ions from the surface zone of concrete in the concomitant presence of chloride ions in the concrete exposed to composite chloride-sulfate solutions with alternating wetting-drying cycles. In case of concrete exposed to chloride solutions, it is observed from Fig. 7.1 to Fig. 7.6 that the free chloride

content of both OPC and PPC concrete increased with increase in concentration of chloride salt in the exposure solution at all depth intervals from the exposure surface, regardless of w/c, presence and type of admixed corrosion inhibitors, and type of chloride salt in the exposure solution. This may be due to the effect of formation of porous C-S-H to a comparatively higher extent in the concrete subjected to solutions with higher concentration of chloride salts due to calcium leaching in the presence of chloride ions that leads to penetration of more amounts of chloride ions into the concrete [195].

7.3.2 Effect of cation type of chloride salt on free chloride ion content and apparent chloride diffusion coefficient of control concrete exposed to chloride solutions

While analyzing the effect of cation type of chloride salt, it is noted that the free chloride ion (C_F) content was mostly higher in the control concrete (without corrosion inhibitors) exposed to NaCl solution than that exposed to CaCl_2 solution followed by MgCl_2 solution for OPC as well as for PPC at both w/c and for all depth intervals as evident from Fig. 7.1, Fig. 7.2 and Appendix B: Fig. B1 and Fig. B2. This might be attributed to the increase in pH value of concrete pore solution in the presence of Na^+ ions, which increased the solubility of Friedel's salt and released the bound chloride. This leads to the availability of more amount of free chloride in the specimens exposed to NaCl solution as compared to those exposed to CaCl_2 and MgCl_2 solutions [52]. The lower free chloride ion content in the concrete exposed to MgCl_2 solution may be ascribed to the dominant effect of penetration of lower amount of chloride ions as compared to that exposed to CaCl_2 solution. The penetration of lower amount of chloride ions in the concrete exposed to MgCl_2 solution may be due to the filling of pores with magnesium hydroxide, which is formed due to reaction of MgCl_2 with calcium hydroxide. The formation of magnesium hydroxide in the concrete exposed to MgCl_2 solution is evident from the XRD patterns shown in Fig. 7.27 and Fig. 7.30, and Appendix B: Fig. B31 and Fig. B34 (discussed in Section 7.5.1.1). In addition, as already stated in Chapter 6, the formation of more amount of calcium hypochlorite (HC) in the concrete exposed to MgCl_2 solution as compared to that exposed to CaCl_2 solution may also be responsible for lower free chloride content in case of exposure to MgCl_2 solution than CaCl_2 solution. From Fig. 7.1, Fig. 7.2 and Appendix B: Fig. B1 and Fig. B2, the free chloride contents of PPC control specimens were higher than OPC control specimens up to depth of 15 mm from the exposure surface irrespective of w/c, and type of chloride salt in the exposure solutions. However, beyond the depth of 15 mm from the exposure surface, the free chloride content was higher in OPC control

specimens as compared to PPC control specimens irrespective of w/c, and type of chloride salt in the exposure solutions. The higher free chloride ion content in the concrete prepared from PPC at lower depth intervals (up to depth of 15 mm) from the exposure surface may be attributed to the formation of denser pore structure in PPC concrete mixes at higher depth intervals (beyond the depth of 15 mm) as compared to OPC concrete mixes. The formation of denser pore structure in PPC concrete at higher depth intervals from the exposure surface reduced the penetration of chloride ions to higher depth intervals and resulted in buildup of chloride ions at lower depth intervals from the exposure surface in the concrete mixes prepared from PPC as compared to OPC. Further, the rate of decrease of chloride penetration with increase in depth from the exposure surface was higher in PPC control concrete as compared to OPC control concrete as observed from the free chloride ion content values shown in Fig. 7.1, Fig. 7.2 and Appendix B: Fig. B1 and Fig. B2. This may be ascribed to the effect of refined pore structure and denser matrix of PPC concrete as a result of formation of additional C-S-H from the pozzolanic reaction [50].

While considering the effect of w/c on free chloride ion (C_F) content, it is noted that the concrete made with lower w/c (i.e., 0.45) mostly exhibited higher free chloride content as compared to higher w/c (i.e., 0.55) at lower depth intervals (i.e., 0-5 mm and 5-10 mm) from the exposure surface irrespective of cement type and type of chloride salt in the exposure solutions. However, at higher depth intervals, i.e., beyond 10 mm from exposure surface, the free chloride content was mostly higher in the concrete prepared with higher w/c than that prepared with lower w/c. This may be attributed to the denser microstructure in concrete prepared with lower w/c as compared to that prepared with higher w/c, which reduced the ingress of chloride ions to higher depth intervals in the concrete. This resulted in accumulation of chloride ions at lower depth intervals from the exposure surface in the concrete made with lower w/c. Further, the rate of ingress of chloride ions with increase in depth from the exposure surface was mostly lower in the concrete made with w/c of 0.45 as compared to that made with w/c of 0.55 regardless of cement type, and chloride salt in the exposure solutions.

From Fig. 7.11 (a), Fig. 7.12 (a), Fig. 7.13 (a), and Fig. 7.14 (a), it is observed that in OPC as well as in PPC control concrete, the apparent chloride diffusion coefficient (D_{app}) mostly increased with increase in concentration of chloride salt in the exposure solution irrespective of w/c and cation type of chloride salt. This may be ascribed to higher concentration gradient of chloride ions (between exposure solution and concrete pore

solution) in the concrete subjected to exposure solution with higher concentration of chloride salt than that subjected to exposure solution with lower concentration of chloride salt. Further, the presence of higher content of chloride ions increases the leaching of calcium from concrete thereby resulting in the formation of porous C-S-H to a comparatively greater degree, which increases the ingress of chloride ions into the concrete exposed to solutions with higher concentration of chloride salt. From Fig. 7.11 (a), Fig. 7.12 (a), Fig. 7.13 (a), and Fig. 7.14 (a), it is noted that the D_{app} of control concrete exposed to NaCl solution was mostly higher as compared to that exposed to $CaCl_2$ solution followed by $MgCl_2$ solution for OPC as well as for PPC at both w/c. This is ascribed to the effect of higher rate of ingress of chloride ions into the concrete exposed to NaCl solution as compared to those exposed to $CaCl_2$ and $MgCl_2$ solutions as indicated by the free chloride ion content values shown in Fig. 7.1, Fig. 7.2, and Appendix B: Fig. B1 and Fig. B2. The observed variation in apparent chloride diffusion coefficient with cation type associated with chloride ions in the present study is similar to that obtained by Song et al. [37]. From Fig. 7.11 (a), Fig. 7.12 (a), Fig. 7.13 (a), and Fig. 7.14 (a), it can be noticed that the D_{app} of PPC control concrete is lower as compared to OPC control concrete. This is attributed to higher resistance against ingress of chloride ions in PPC concrete as compared to OPC concrete as a result of optimization of the microstructure of capillary pores in PPC concrete due to formation of additional C-S-H in the pozzolanic reaction [195, 196]. The average ratio of apparent chloride diffusion coefficient of OPC control concrete to that of PPC control concrete is 3.21 irrespective of w/c, and cation type and concentration of chloride salt in the exposure solutions. Further, with increase in w/c, the apparent chloride diffusion coefficient mostly increased in control concrete exposed to chloride solutions irrespective of cement type and chloride salt in the exposure solution. This may be due to the fact that the formation of porous microstructure in the concrete at higher w/c increased the ingress of chloride ions thereby resulting in higher apparent chloride diffusion coefficient of concrete [196].

7.3.3 Effect of cation type of chloride salt on free chloride ion content and apparent chloride diffusion coefficient of control concrete exposed to composite chloride-sulfate solutions

From Fig. 7.7 (a), Fig. 7.8 (a), Fig. 7.9 (a) and Fig. 7.10 (a), it is observed that the sulfate ions significantly influenced the free chloride ion (C_F) content of control concrete (without corrosion inhibitors) exposed to composite chloride-sulfate solutions with respect to cation

type of chloride ions. From the obtained results, the free chloride ion (C_F) content is mostly higher in the concrete exposed to $\text{CaCl}_2 + \text{MgSO}_4$ solution as compared to $\text{NaCl} + \text{MgSO}_4$ solution followed by $\text{MgCl}_2 + \text{MgSO}_4$ solution at all depth intervals, irrespective of cement type, w/c, and type of chloride salt in the composite chloride-sulfate solutions. The higher free chloride ion content in the specimens exposed to $\text{CaCl}_2 + \text{MgSO}_4$ solution may be ascribed to the release of bound chloride due to decomposition of Friedel's salt to a higher extent in the presence of sulfate ions [61]. The lower free chloride ion content in the concrete exposed to $\text{MgCl}_2 + \text{MgSO}_4$ solution as compared to other two composite chloride-sulfate solutions may be attributed to the effect of formation of higher amount of brucite (magnesium hydroxide) in the concrete exposed to $\text{MgCl}_2 + \text{MgSO}_4$ solution, which might have filled the pores in concrete to a certain extent thereby reducing the penetration of chloride ions into concrete [197]. The formation of higher amount of magnesium hydroxide ($\text{Mg}(\text{OH})_2$) in the concrete exposed to $\text{MgCl}_2 + \text{MgSO}_4$ solution as compared to other two composite chloride-sulfate solutions was also evident from the results of XRD analysis shown in Fig. 7.33 and Fig. 7.36. Further, the lower pH of concrete in case of exposure to $\text{MgCl}_2 + \text{MgSO}_4$ solution might have resulted in release of lower amount of chloride ions from Friedel's salt [47, 197]. From Fig. 7.7 (a), Fig. 7.8 (a), Fig. 7.9 (a) and Fig. 7.10 (a), it is observed that the free chloride ion (C_F) content of PPC control concrete was higher as compared to OPC control concrete up to a depth of 15 mm from the exposure surface whereas, beyond the depth of 15 mm from the exposure surface, the free chloride content was higher in OPC control concrete as compared to PPC control concrete, irrespective of w/c, and type of chloride salt in the composite chloride-sulfate solutions. The similar variation in free chloride content with cement type was also observed in case of control concrete (without corrosion inhibitors) exposed to only chloride solutions and the reason for the same is already explained earlier. Between the w/c, at lower depth intervals i.e., up to 10 mm from the exposure surface, the free chloride ion content was mostly higher in the concrete prepared with w/c of 0.45 than that prepared with w/c of 0.55 irrespective of cement type and type of chloride salt in the composite chloride-sulfate solutions. However, beyond the depth of 10 mm from the exposure surface, the concrete made with higher w/c (0.55) mostly exhibited higher free chloride content as compared to that made with lower w/c (0.45). As explained earlier, the variation in concrete microstructure with change in w/c may be the reason for the variation in free chloride content in the concrete between the w/c. Besides, the rate of ingress of chloride ions with increase in depth was mostly higher in the concrete made with w/c of 0.55 than that made with w/c of 0.45 irrespective of

cement type, and chloride salt in the composite solutions. While comparing between only chloride, and composite chloride-sulfate solutions, the free chloride ion content of control concrete was mostly lower in case of exposure to composite chloride-sulfate solutions as compared to chloride solutions at all depth intervals irrespective of cement type, w/c and cation type of chloride salt in the exposure solutions. The lower free chloride ion content in the concrete exposed to composite chloride-sulfate solutions may be due to the dominant effect of filling of concrete pores with brucite (magnesium hydroxide), which might have reduced the ingress of chloride ions into concrete.

From Fig. 7.15 and Fig. 7.16, it is inferred that the apparent chloride diffusion coefficient (D_{app}) was higher in the control concrete exposed to $MgCl_2+MgSO_4$ solution in comparison to $NaCl+MgSO_4$ solution followed by $CaCl_2+MgSO_4$ solution irrespective of cement type and w/c. Although, the free chloride content was lower in the concrete exposed to $MgCl_2+MgSO_4$ solution as compared to other composite chloride-sulfate solutions, the higher D_{app} in case of exposure to $MgCl_2+MgSO_4$ solution may be due to the effect of relatively higher rate of ingress of chloride ions from lower depth intervals to higher depth intervals from the exposure surface of concrete thereby resulting in a comparatively lower difference in free chloride content between lower depth and higher depth intervals. The same reason may be attributed for the variation in D_{app} of concrete between $NaCl+MgSO_4$ and $CaCl_2+MgSO_4$ solutions. From Fig. 7.15 and Fig. 7.16, it is observed that the variations in D_{app} of concrete with cement type and w/c in case of exposure to composite chloride-sulfate solutions are similar to that observed in case of concrete exposed to only chloride solutions. In case of exposure to composite chloride-sulfate solutions, the average ratio of apparent chloride diffusion coefficient of OPC control concrete to that of PPC control concrete is 1.88 irrespective of w/c, and cation type of chloride salt in the exposure solution. While evaluating the effect of sulfate ion on apparent chloride diffusion coefficient (D_{app}), it is observed that D_{app} was mostly higher in the concrete exposed to chloride solutions as compared to that exposed to composite chloride-sulfate solutions irrespective of cement type, w/c, and type of chloride salt in the exposure solutions. The lower D_{app} in the concrete exposed to composite chloride-sulfate solutions may be attributed to the effect of lower rate of penetration of chloride ions from lower depth intervals to higher depth intervals from the exposure surface of concrete.

7.3.4 Effect of corrosion inhibitors on free chloride ion content and apparent chloride diffusion coefficient of concrete exposed to chloride solutions

From Fig. 7.1 to Fig. 7.6 and Appendix B: Fig. B1 to Fig. B6, it is observed that the free chloride ion (C_F) content of concrete containing corrosion inhibitors is mostly lower than that of control concrete (without corrosion inhibitors) at all depth intervals irrespective of cement type, w/c, and type of chloride salt in the exposure solution. The formation of nitrite-AFm (due to reaction of NO_2^- ions with AFm (aluminate-ferrite-monosubstituent) phase of hydrated cement [132, 198]) might have blocked the pores of concrete and reduced the penetration of chloride ions into the concrete admixed with NaNO_2 as compared to control concrete. Further, the chloride ions partially replace the NO_2^- ions in nitrite-AFm to form Friedel's salt that increases the chloride binding and reduces the free chloride content in the concrete admixed with NaNO_2 [132] as compared to control concrete. As stated earlier, the reaction of phosphate ions with chloride and Ca^{2+} ions forms chlorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{Cl}$) [189], which results in binding of chloride ions thereby reducing free chloride ion content in the concrete admixed with DHP as compared to control concrete. From Fig. 7.3 to Fig. 7.6 and Appendix B: Fig. B3 to Fig. B6, it is noticed that the free chloride ion content of concrete exposed to NaCl solution is mostly higher as compared to that exposed to CaCl_2 and MgCl_2 solutions for both OPC and PPC in the presence of corrosion inhibitors at both w/c. In case of NaNO_2 , the reason behind higher free chloride ion content in the concrete subjected to NaCl solution is attributed to the effect of replacement of adsorbed NO_2^- ions from the surface of cement hydration products such as C-S-H by chloride ions to a comparatively lower extent than that in the concrete exposed to CaCl_2 and MgCl_2 solutions. This leads to availability of more C_F content in concrete in the presence of NaCl [117]. In the concrete mixes admixed with DHP, the formation of chlorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{Cl}$) due to reaction of phosphate ions with chloride and Ca^{2+} ions, to a comparatively lower extent in the presence of NaCl might have resulted in lower extent of chloride binding thereby leading to higher free chloride content in the concrete mixes in the presence of NaCl as compared to that in the presence of CaCl_2 and MgCl_2 . The free chloride ion (C_F) content of OPC and PPC concrete mixes irrespective of w/c and admixed corrosion inhibitors mostly decreased in the order C_F : $\text{NaCl} > \text{CaCl}_2 > \text{MgCl}_2$.

While analyzing the effect of NaNO_2 and DHP, it is observed that the free chloride ion (C_F) content for OPC concrete is mostly higher in the specimens containing NaNO_2 than those containing DHP when exposed to NaCl and CaCl_2 solutions at all depth intervals for both

w/c. However, in case of exposure to MgCl_2 solution, the C_F content is mostly higher in DHP specimens as compared to NaNO_2 specimens. For PPC, the specimens admixed with NaNO_2 mostly showed higher C_F content as compared to those admixed with DHP at all depth intervals irrespective of w/c and chloride salt in the exposure solutions. The higher free chloride content in the concrete containing NaNO_2 may be due to the effect of adsorption of NO_2^- ions on cement hydration products, which limited the availability of cement hydration products for chloride binding [117]. Similar to the control specimens (without corrosion inhibitors), in the specimens containing corrosion inhibitors, the C_F content is mostly higher in PPC concrete up to the depth of 15 mm from the surface of exposure than OPC concrete at both w/c and irrespective of cation type of chloride salt in the exposure solution. After that, i.e., beyond the depth of 15 mm from the surface of exposure, the C_F content is mostly higher in OPC concrete as compared to PPC concrete. The lower amount of C_F at higher depth intervals from the surface of exposure in PPC concrete is ascribed to the effect of higher resistance against ingress of chloride ions due to formation of compacted pore structure in PPC concrete (as stated earlier) in comparison to OPC concrete [195, 196]. From Fig. 7.3 to Fig. 7.6 and Appendix B: Fig. B3 to Fig. B6, it is observed that the concrete made with w/c of 0.45 mostly exhibited higher C_F content at lower depth intervals (i.e., up to 10 mm) from the exposure surface of concrete irrespective of cement type, corrosion inhibitor and type of chloride salt in the exposure solutions. However, at higher depth intervals i.e., beyond 10 mm from the exposure surface, the C_F content was mostly higher in the concrete prepared with w/c of 0.55. The reason for this variation in free chloride ion (C_F) content of concrete with change in w/c was already explained in Section 7.3.2.

From Fig. 7.11 (b, c), Fig. 7.12 (b, c), Fig. 7.13 (b, c), and Fig. 7.14 (b, c), it is observed that the apparent chloride diffusion coefficient (D_{app}) of concrete admixed with corrosion inhibitors mostly increased with increase in chloride salt concentration regardless of cement type, w/c and cation type of chloride salt in the exposure solution. The D_{app} of the concrete containing corrosion inhibitors is lower than that of control concrete (without corrosion inhibitors) exposed to different exposure solutions for both cements and both w/c as noted from Fig. 7.11 to Fig. 7.14. In the presence of NaNO_2 , the filling of pores of concrete with nitrite-AFm might have reduced the diffusion of chloride ions into the concrete [132, 198]. Similarly, in the presence of DHP, the phosphate ions react with portlandite (calcium hydroxide) and form insoluble calcium phosphate, which can block the concrete pores and

decrease the diffusion of chloride ions into concrete [25, 96, 131]. The average ratios of apparent chloride diffusion coefficient of OPC control concrete to that of OPC concrete containing NaNO_2 , and DHP are 2.20 and 2.04 respectively irrespective of w/c, and cation type and concentration of chloride salt in the exposure solutions. Similarly, the average ratios of apparent chloride diffusion coefficient of PPC control concrete to that of PPC concrete containing NaNO_2 , and DHP are 1.82 and 1.80 respectively.

Further, it has been observed that in both OPC and PPC concrete mixes containing corrosion inhibitors, the D_{app} of the specimens exposed to NaCl solution is mostly higher as compared to CaCl_2 solution followed by the specimens exposed to MgCl_2 solution irrespective of w/c and type of corrosion inhibitor. From Fig. 7.11 (b, c), Fig. 7.12 (b, c), Fig. 7.13 (b, c), and Fig. 7.14 (b, c), it is noted that for OPC, the concrete containing DHP mostly showed higher D_{app} as compared to that containing NaNO_2 regardless of w/c, and cation type of chloride salt in the exposure solution. However, as stated earlier, the free chloride ion (C_F) content was mostly lower in the concrete containing DHP than that containing NaNO_2 . The higher apparent chloride diffusion coefficient of concrete containing DHP is attributed to the effect of relatively higher rate of penetration of chloride ions from lower depth interval to higher depth intervals from the exposure surface of concrete containing DHP as compared to that containing NaNO_2 , which is evident from the free chloride ion content profile shown in Fig. 7.3 to Fig. 7.6, and Appendix B: Fig. B3 to Fig. B6. In case of PPC concrete, there was no systematic variation in apparent chloride diffusion coefficient of concrete between NaNO_2 and DHP irrespective of w/c, and cation type of chloride salt in the exposure solution. This may be attributed to the effect of unsystematic variation in the rate of ingress of chloride ions from lower depth interval to higher depth intervals from the exposure surface of concrete between NaNO_2 and DHP for PPC concrete. Further, the apparent chloride diffusion coefficient of OPC concrete is higher than PPC concrete irrespective of w/c, admixed corrosion inhibitor, and chloride salt in the exposure solution, as noted from Fig. 7.11 (b, c), Fig. 7.12 (b, c), Fig. 7.13 (b, c), and Fig. 7.14 (b, c). The average ratio of apparent chloride diffusion coefficient of OPC concrete containing NaNO_2 to that of PPC concrete containing NaNO_2 is 2.03 irrespective of w/c, and cation type and concentration of chloride salt in the exposure solution. Similarly, the average ratio of apparent chloride diffusion coefficient of OPC concrete containing DHP to that of PPC concrete containing DHP is 2.25. The apparent chloride diffusion coefficient

of concrete containing corrosion inhibitors mostly increased with increase in w/c in case of exposure to chloride solutions regardless of cement type, and type of corrosion inhibitor.

7.3.5 Effect of corrosion inhibitors on free chloride ion content and apparent chloride diffusion coefficient of concrete exposed to composite chloride-sulfate solutions

From Fig. 7.7 to Fig. 7.10, it is observed that the concrete containing corrosion inhibitors mostly showed lower free chloride ion (C_F) content as compared to control concrete (without corrosion inhibitors) at all depth intervals regardless of cement type, w/c, and chloride salt in the composite chloride-sulfate solutions. The reason behind lower free chloride content in the concrete containing corrosion inhibitors was already explained in Section 7.3.4. Further, in the presence of corrosion inhibitors, the concrete mixes exposed to $\text{CaCl}_2 + \text{MgSO}_4$ solution mostly showed higher C_F content as compared to that exposed to $\text{NaCl} + \text{MgSO}_4$ solution followed by $\text{MgCl}_2 + \text{MgSO}_4$ solution irrespective of cement type, w/c, and corrosion inhibitors. The similar variation in free chloride content among composite chloride-sulfate solutions was also observed in case of control concrete mixes (without corrosion inhibitors) and the reason for the same was already discussed in Section 7.3.3. This indicates that the presence of corrosion inhibitors did not affect the variation in free chloride content among different composite chloride-sulfate solutions. While comparing between NaNO_2 and DHP, it is observed that the free chloride ion content was mostly higher in the concrete admixed with DHP as compared to that admixed with NaNO_2 at all depth intervals irrespective of cement type, w/c, and cation type of chloride salt in the composite chloride-sulfate solutions. This may be due to the ingress of higher amount of chloride ions into the concrete containing DHP as compared to that containing NaNO_2 in the presence of sulfate ions. Further, the variations in free chloride content of concrete containing corrosion inhibitors with cement type and w/c were similar to that observed in case of control concrete (without corrosion inhibitors) exposed to composite chloride-sulfate solutions.

While comparing only chloride, and composite chloride-sulfate solutions, it is inferred that the free chloride content of concrete containing corrosion inhibitors was mostly higher in case of exposure to composite chloride-sulfate solutions as compared to chloride solutions at all depth intervals irrespective of cement type, w/c, corrosion inhibitor, and cation type of chloride salt in the exposure solutions (From Fig. 7.3 to Fig. 7.6, Fig. 7.7 (b, c), Fig. 7.8 (b, c), Fig. 7.9 (b, c), Fig. 7.10 (b, c), and Appendix B: Fig. B3 to Fig. B6). Although, the concrete pores might have filled with brucite (magnesium hydroxide) to a certain extent in

case of exposure to composite chloride-sulfate solutions, the dominant effect of higher extent of chloride binding in the concrete exposed to only chloride solutions in the presence of corrosion inhibitors resulted in lower free chloride content.

From Fig. 7.15 and Fig. 7.16, the apparent chloride diffusion coefficient (D_{app}) of concrete admixed with corrosion inhibitors was lower than that of control concrete (without corrosion inhibitors) in case of exposure to composite chloride-sulfate solutions irrespective of cement type, w/c, corrosion inhibitor and chloride salt in the exposure solutions. This may be attributed to the blocking effect of corrosion inhibitors that reduced the ingress of chloride ions into concrete thereby decreasing the apparent chloride diffusion coefficient of concrete admixed with corrosion inhibitor as compared to control concrete. In case of exposure to composite chloride-sulfate solutions, the average ratios of apparent chloride diffusion coefficient of OPC control concrete to that of OPC concrete containing NaNO_2 , and DHP are 1.42 and 1.34 respectively irrespective of w/c, and cation type of chloride salt in the exposure solutions. Similarly, the average ratios of apparent chloride diffusion coefficient of PPC control concrete to that of PPC concrete containing NaNO_2 , and DHP are 1.06 and 1.10 respectively.

In the concrete mixes admixed with corrosion inhibitors and exposed to composite chloride-sulfate solutions, the variation in apparent chloride diffusion coefficient among the three chloride salts is similar to that as observed in case of control concrete (without corrosion inhibitors) exposed to composite chloride-sulfate solutions. Further, the concrete containing DHP mostly showed higher D_{app} as compared to that containing NaNO_2 regardless of cement type, w/c, and cation type of chloride salt in case of exposure to composite chloride-sulfate solutions. This is attributed to higher rate of chloride ingress into the concrete admixed with DHP as compared to that admixed with NaNO_2 . Between the cements, the PPC concrete mixes showed lower D_{app} as compared to OPC concrete mixes irrespective of w/c, corrosion inhibitor, and chloride salt in the composite chloride-sulfate solutions. In the presence of NaNO_2 , the average ratio of apparent chloride diffusion coefficient of OPC concrete to that of PPC concrete is 1.40 irrespective of w/c, and cation type of chloride salt in the composite chloride-sulfate solutions. Similarly, in the presence of DHP, the average ratio of apparent chloride diffusion coefficient of OPC concrete to that of PPC concrete is 1.53. Further, the apparent chloride diffusion coefficient of concrete mostly increased with increase in w/c in case of exposure to composite chloride-sulfate solutions for both cements, and both corrosion inhibitors. From Fig. 7.11 (b, c), Fig. 7.12

(b, c), Fig. 7.13 (b, c), Fig. 7.14 (b, c), Fig. 7.15, and Fig. 7.16, it is observed that the apparent chloride diffusion coefficient (D_{app}) was higher in the concrete exposed to composite chloride-sulfate solutions as compared to that exposed to only chloride solutions regardless of cement type, w/c, corrosion inhibitors, and type of chloride salt in the exposure solutions. The higher chloride diffusion coefficient in case of exposure to composite chloride-sulfate solutions may be ascribed to the effect of higher rate of ingress of chloride ions from lower depth to higher depth intervals from the exposure surface of concrete. It may be noted that, as stated earlier, the free chloride content of concrete containing corrosion inhibitors was mostly higher in case of exposure to composite chloride-sulfate solutions as compared to only chloride solutions.

7.4 Chloride binding capacity of concrete

As stated in Chapter 3, modified Langmuir, and Freundlich isotherms were applied to the obtained free chloride (% by weight of concrete) and bound chloride (% by weight of concrete) contents. Typical plots showing the modified Langmuir and Freundlich isotherms between free chloride and bound chloride ion contents are shown in Fig. 7.17 to Fig. 7.19. The free chloride and bound chloride ion contents shown in these figures correspond to the concrete powder samples collected from different depth intervals from the exposure surface of the specimens. From the obtained plots, it is observed that the modified Langmuir and Freundlich binding isotherms are not fitting well to the free and bound chloride ion contents as the coefficient of correlation (R^2) values are much less than 1.0 in most of the cases for both the isotherms except in very few cases where the coefficient of correlation (R^2) values are above 0.80. Further, for both the isotherms, there is no consistent variation in the values of binding constants i.e., α and β between cement type, cation type of chloride salt, and corrosion inhibitors. This may be attributed to the dominant effect of unsystematic variation in bound chloride ion content with respect to free chloride ion content at different depth intervals from the exposure surface of the specimens.

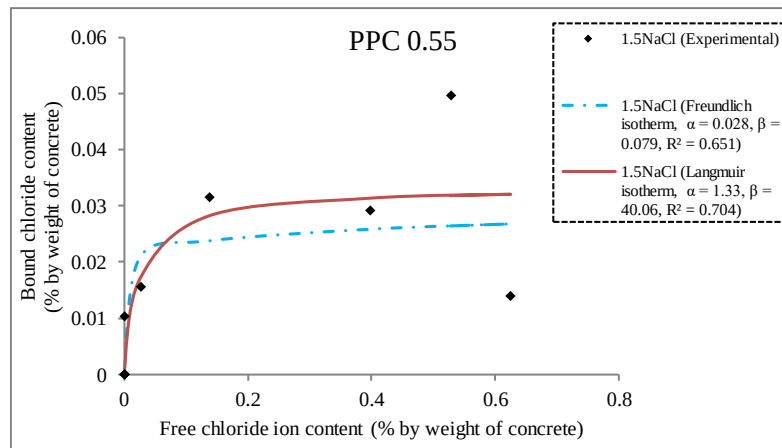


Fig. 7.17 Freundlich and Langmuir isotherms between free and bound chloride contents for PPC control concrete (without corrosion inhibitors) exposed to 1.5% NaCl solution

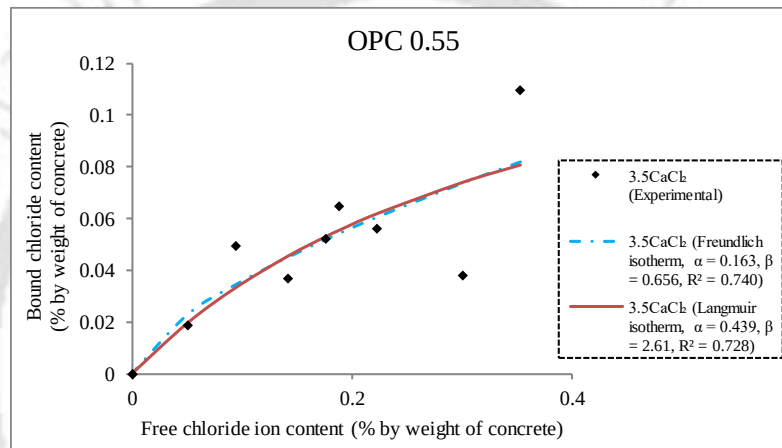


Fig. 7.18 Freundlich and Langmuir isotherms between free and bound chloride contents for OPC control concrete (without corrosion inhibitors) exposed to 3.5% CaCl₂ solution

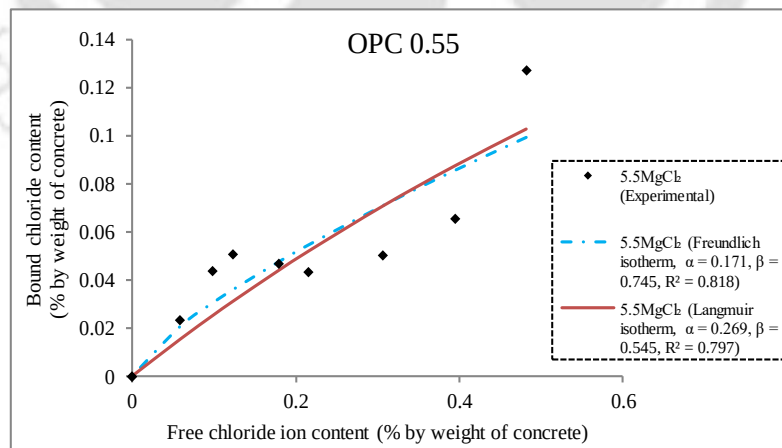


Fig. 7.19 Freundlich and Langmuir isotherms between free and bound chloride contents for OPC control concrete (without corrosion inhibitors) exposed to 5.5% MgCl₂ solution

As stated in Chapter 3, the chloride binding capacity (R) of concrete mixes prepared from OPC and PPC was determined from the linear relationship between the experimentally

obtained free chloride ion (C_F) content and total chloride ion (C_T) content. The existence of linear relationship between free and total chloride in the concrete subjected to external exposure may be attributed to the effect of chloride and hydroxide ion gradient that results in leaching of hydroxide ions from concrete at a rate similar to that of ingress of chloride ions into the concrete [199]. Typical plots showing the relationship between free chloride ion (C_F) content and total chloride ion (C_T) content of OPC and PPC control concrete, and those admixed with corrosion inhibitors at both w/c and exposed to chloride, and composite chloride-sulfate solutions are shown in Fig. 7.20 to Fig. 7.22. The remaining plots are shown in Appendix B: Fig. B7 to Fig. B30.

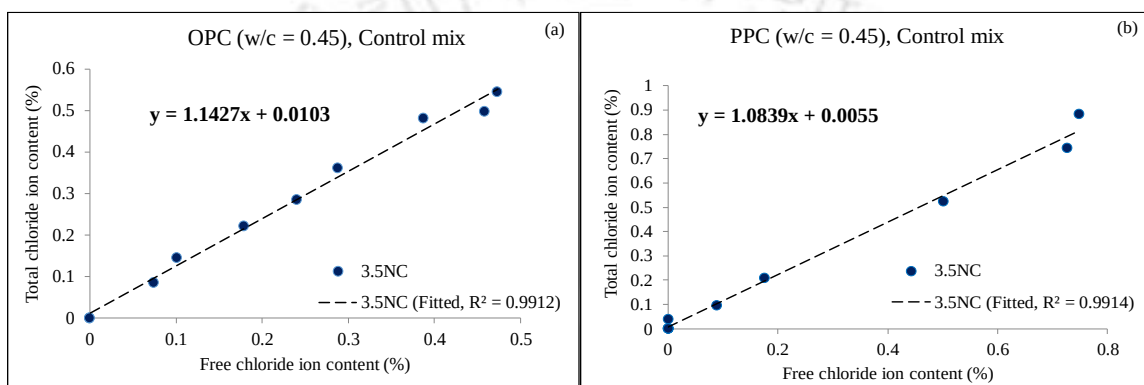


Fig. 7.20 Relationship between free chloride ion and total chloride ion contents of control concrete (without corrosion inhibitors) at w/c of 0.45 and exposed to 3.5% NaCl solution: (a) OPC, and (b) PPC

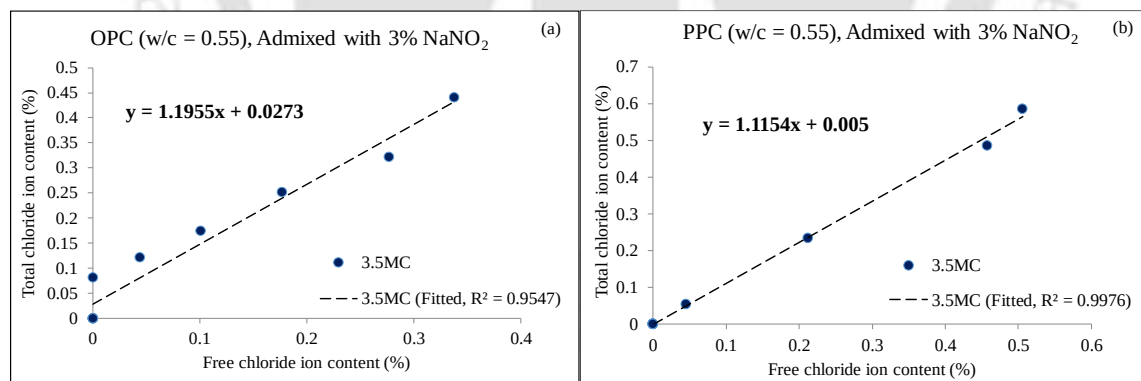


Fig. 7.21 Relationship between free chloride ion and total chloride ion contents of concrete containing 3% NaNO₂ at w/c of 0.55 and exposed to 3.5% MgCl₂ solution: (a) OPC, and (b) PPC

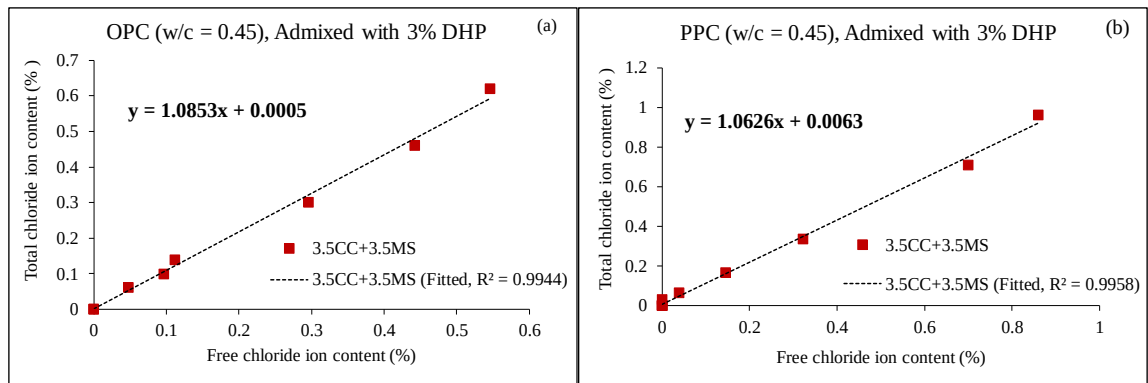


Fig. 7.22 Relationship between free chloride ion and total chloride ion contents of concrete containing 3% DHP at w/c of 0.45 and exposed to 3.5% CaCl₂+3.5% MgSO₄ solution: (a) OPC, and (b) PPC

From the obtained linear relationship (Eq. 3.8, Chapter 3), the value of the coefficient α was calculated followed by determining the chloride binding capacity (R) of different concrete mixes. The obtained values of chloride binding capacity (R) of concrete mixes exposed to only chloride solutions are shown in Fig. 7.23 and Fig. 7.24.

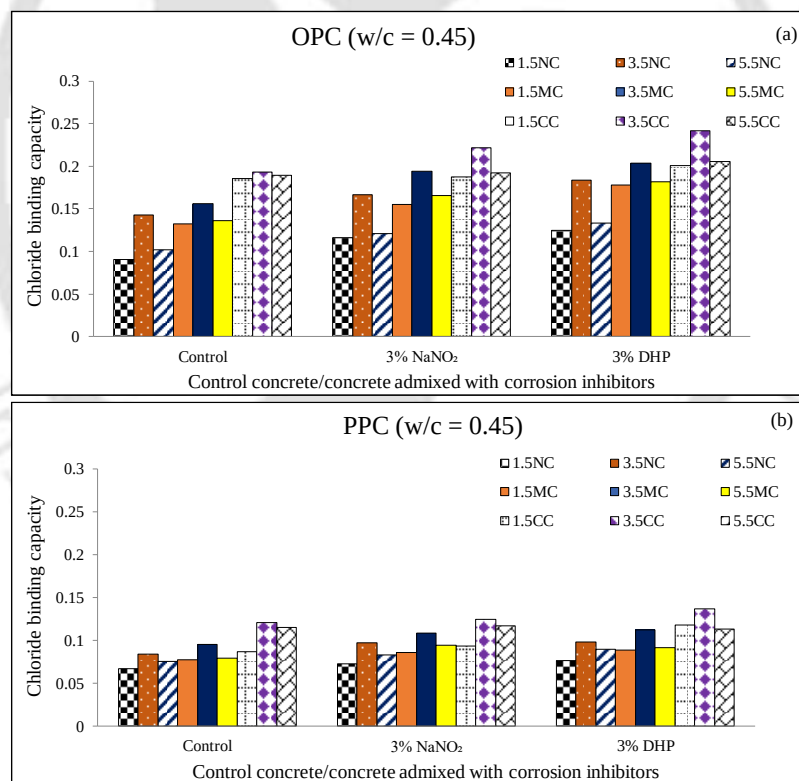


Fig. 7.23 Chloride binding capacity of concrete at w/c of 0.45 and exposed to different chloride salt solutions: (a) OPC, and (b) PPC

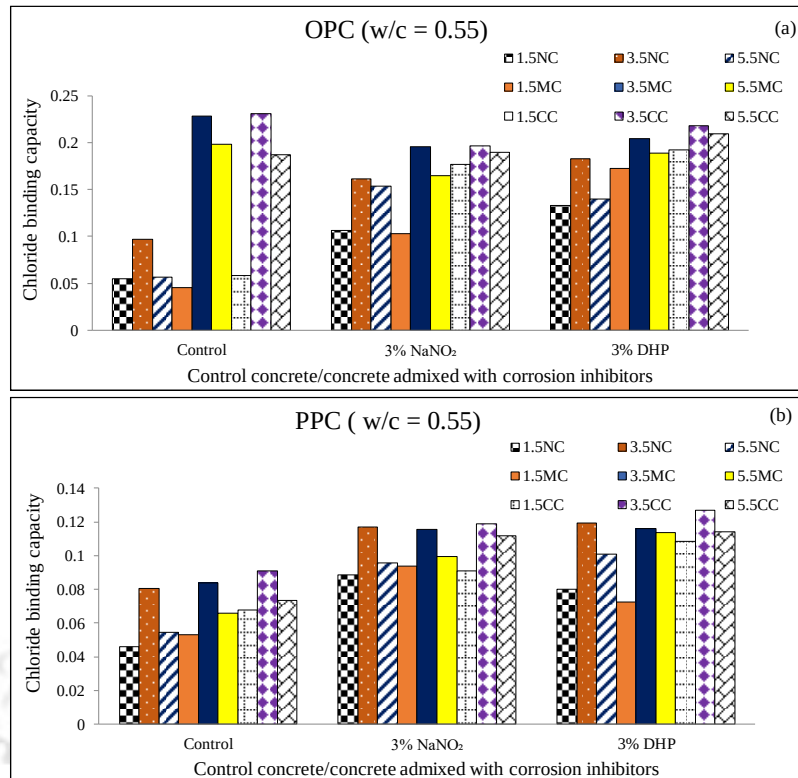


Fig. 7.24 Chloride binding capacity of concrete at w/c of 0.55 and exposed to different chloride salt solutions: (a) OPC, and (b) PPC

From Fig. 7.23 and Fig. 7.24, it is observed that for both OPC and PPC, the chloride binding capacity (R) of concrete admixed with corrosion inhibitors is mostly higher as compared to the control concrete (without corrosion inhibitors) irrespective of w/c, corrosion inhibitor, and type of chloride salt in the exposure solutions. This may be due to the effect of less diffusion of chloride ions into the concrete containing corrosion inhibitors as compared to the control concrete as well as binding of chloride ions with hydrated cement phases of concrete to a comparatively higher degree in the presence of corrosion inhibitors as compared to control concrete. The higher extent of chloride binding in the concrete admixed with corrosion inhibitors as compared to control concrete is also in line with the formation of calcium chloroaluminate (CCA) as evident from the weight (%) of CCA obtained from the XRD analysis, as shown in Fig. 7.39 to Fig. 7.42 (discussed later in Section 7.5.1.2). While comparing among the cation type of chloride salts, the chloride binding capacity (R) is mostly higher in the concrete exposed to CaCl₂ solution than MgCl₂ solution followed by NaCl solution for OPC as well as for PPC irrespective of w/c, and presence of corrosion inhibitors. The higher chloride binding capacity (R) in the concrete exposed to CaCl₂ solution as compared to MgCl₂ and NaCl solutions may be ascribed to the significant effect of binding of chloride ions with C₃A to a greater extent thereby

resulting in the formation of more amount of calcium chloroaluminate (CCA) in the concrete exposed to CaCl_2 solution as compared to MgCl_2 and NaCl solutions. The formation of more amount of calcium chloroaluminate (CCA) in the concrete exposed to CaCl_2 solution as compared to MgCl_2 solution followed by NaCl solution is corroborated with the weight (%) of calcium chloroaluminate obtained from the XRD analysis, as shown in Fig. 7.39 to Fig. 7.42. Further, the variation in chloride binding capacity (R) of concrete exposed to different chloride salt solutions may also be attributed to the variations in the extent of physical binding of chloride ions with C-S-H, which is dependent on the pH of concrete pore solution. In case of exposure to MgCl_2 and CaCl_2 solutions, the presence of MgCl_2 and CaCl_2 causes the precipitation of $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ respectively in the concrete that decreases the $(\text{OH})^-$ concentration and pH of electrolytic pore solution of concrete. The physical binding of chloride ions with cement hydration products takes place through competing adsorption between chloride ions and $(\text{OH})^-$ ions. Thus, decrease in the $(\text{OH})^-$ concentration in the concrete pore solution increases the physical binding of chloride ions with the C-S-H in the concrete exposed to MgCl_2 and CaCl_2 solutions as compared to NaCl solution [56]. Further, between CaCl_2 and MgCl_2 solutions, the effect of physical binding of chloride ions with C-S-H to a comparatively higher degree in the concrete exposed to CaCl_2 solution over the effect of lower extent of chloride binding with M-S-H produced in the concrete exposed to MgCl_2 solution might have also resulted in higher extent of chloride binding in the concrete exposed to CaCl_2 solution as compared to that exposed to MgCl_2 solution, in addition to the effect of chemical binding of chloride ions with C_3A . From Fig. 7.23 and Fig. 7.24, it can be noted that the chloride binding capacity of both control concrete and that admixed with corrosion inhibitors is higher in case of exposure to solutions with 3.5% chloride salt concentration followed by exposure to solutions with 5.5%, and 1.5% chloride salt concentrations irrespective of cement type, w/c and cation type of chloride salt. This may be due to the significant effect of reaction of chloride ions with C_3A to a comparatively higher degree in case of exposure to chloride solutions with 3.5% chloride salt concentration owing to the ingress of chloride ions that led to binding with the available C_3A to a comparatively greater degree as compared to 5.5% and 1.5% chloride salt concentrations.

From Fig. 7.23 and Fig. 7.24, it is noted that the chloride binding capacity of the concrete containing DHP is mostly higher than that containing NaNO_2 for OPC as well as for PPC irrespective of w/c and cation type of chloride salt in the exposure solution. In case of

concrete containing NaNO_2 , the NO_2^- ions are bound chemically with AFm to form nitrite-AFm as well as physically adsorbed on the surface of cement hydration products. Although the ingress of chloride ions partially replaces the NO_2^- ions in nitrite-AFm to form Friedel's salt, the dominant effect of partial replacement of adsorbed NO_2^- ions from C-S-H by chloride ions results in lower extent of physical binding of chloride ions with C-S-H in the concrete admixed with NaNO_2 than that admixed with DHP [117, 132, 198]. In case of concrete admixed with DHP, the formation of chlorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{Cl}$) might have resulted in higher chloride binding as compared to that admixed with NaNO_2 [189]. From Fig. 7.23 and Fig. 7.24, it is observed that the chloride binding capacity (R) of OPC concrete mixes is higher as compared to PPC concrete mixes irrespective of w/c, presence and type of admixed corrosion inhibitors, and chloride salt in the exposure solutions. This may be due to the significant effect of reaction of chloride ions with C_3A to a greater extent due to the availability of higher C_3A content in OPC concrete than that in PPC concrete. The reaction of chloride ions with C_3A to a higher extent resulted in the formation of more amount of calcium chloroaluminate (CCA) in OPC concrete, which is corroborated with the variations in the formation of CCA as evident from its weight (%) obtained from the XRD analysis, shown in Fig. 7.39 to Fig. 7.42. While comparing the effect of w/c on chloride binding capacity, it is observed that the control concrete (without corrosion inhibitors) prepared with lower w/c (0.45) mostly showed higher chloride binding capacity as compared to that made with higher w/c (0.55) irrespective of cement type, and cation type of chloride salt (Fig. 7.23 and Fig. 7.24). Although the ingress of chloride ions was comparatively lower in the concrete prepared with lower w/c as compared to higher w/c, the dominant effect of higher extent physical binding of chloride ions with C-S-H in the concrete prepared with lower w/c resulted in higher chloride binding capacity of concrete. In case of concrete admixed with corrosion inhibitors, there was no systematic variation in chloride binding capacity of concrete with w/c irrespective of cement type, type of corrosion inhibitor, and cation type of chloride salt in the exposure solution. This may be attributed to the effect of alterations in the extent of reaction of chloride ions with hydrated cement phases over different depth intervals with change in w/c of concrete in the presence of corrosion inhibitors.

The obtained values of chloride binding capacity (R) of concrete mixes exposed to composite chloride-sulfate solutions are shown in Fig. 7.25 and Fig. 7.26.

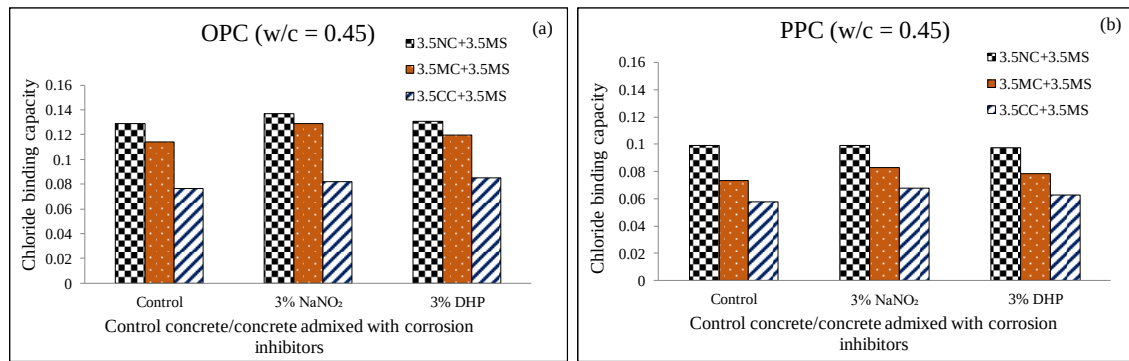


Fig. 7.25 Chloride binding capacity of concrete at w/c of 0.45 and exposed to different composite chloride-sulfate solutions: (a) OPC, and (b) PPC

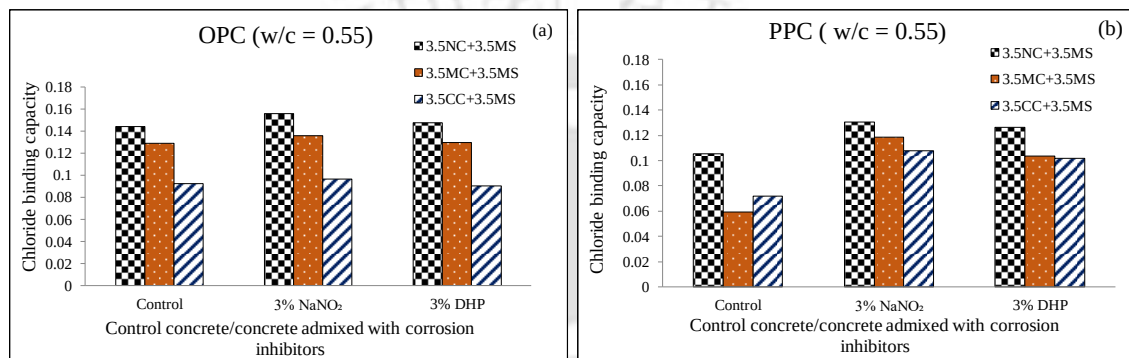


Fig. 7.26 Chloride binding capacity of concrete at w/c of 0.55 and exposed to different composite chloride-sulfate solutions: (a) OPC, and (b) PPC

From Fig. 7.25 and Fig. 7.26, it is observed that the chloride binding capacity (R) of concrete admixed with corrosion inhibitors was higher as compared to control concrete in case of exposure to composite chloride-sulfate solutions irrespective of cement type, w/c, corrosion inhibitor and type of chloride salt. This may be ascribed to the effect of lower ingress of chloride ions as well as higher extent of binding of chloride ions with hydrated cement phases in the concrete containing corrosion inhibitors as compared to control concrete. While comparing the effect of cation type of chloride salt, it is noted that the chloride binding capacity was higher in the concrete exposed to NaCl+MgSO₄ solution as compared to MgCl₂+MgSO₄ followed by CaCl₂+MgSO₄ solutions for control concrete (without corrosion inhibitors) as well as those admixed with corrosion inhibitors, irrespective of cement type, and w/c. In case of concrete exposed to NaCl+MgSO₄ solution, the higher chloride binding capacity may be attributed to the effect of formation of comparatively more amount of calcium chloroaluminate (Friedel's salt) in the concomitant presence of chloride and sulfate ions as compared to MgCl₂+MgSO₄ and CaCl₂+MgSO₄ solutions. The formation of higher amount of calcium chloroaluminate in the concrete exposed to NaCl+MgSO₄ solution than other two composite chloride-sulfate solutions is in

line with its weight (%) obtained from the XRD analysis, as shown in Fig. 7.43 and Fig. 7.44. The lower chloride binding capacity in case of exposure to $\text{CaCl}_2 + \text{MgSO}_4$ solution may be ascribed to the decomposition of Friedel's salt to a comparatively higher extent in the presence of sulfate ions [61]. The higher chloride binding capacity of concrete exposed to $\text{MgCl}_2 + \text{MgSO}_4$ solution as compared to $\text{CaCl}_2 + \text{MgSO}_4$ solution may be attributed to the effect of formation of more quantity of calcium hypochlorite and calcium chloroaluminate in the concrete exposed to $\text{MgCl}_2 + \text{MgSO}_4$ solution than $\text{CaCl}_2 + \text{MgSO}_4$ solution. The formation of higher amount of calcium hypochlorite and calcium chloroaluminate in the concrete exposed to $\text{MgCl}_2 + \text{MgSO}_4$ solution than $\text{CaCl}_2 + \text{MgSO}_4$ solution are evident from the results of XRD analysis (discussed later in Section 7.5.1.1).

From Fig. 7.25 and Fig. 7.26, it is observed that the concrete containing DHP mostly showed lower chloride binding capacity than that containing NaNO_2 irrespective of cement type, w/c and chloride salt in the composite chloride-sulfate solutions. This may be attributed to the effect of alterations in the extent of formation of chlorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{Cl}$) as well as that in the extent of physical binding of chloride ions with C-S-H in the concomitant presence of chloride and sulfate ions in the concrete containing DHP. Further, in case of exposure to composite chloride-sulfate solutions, the variation in chloride binding capacity (R) of concrete with cement type was similar to that in case of exposure to only chloride solutions as observed from Fig. 7.23 to Fig. 7.26. While comparing the effect of w/c, the concrete prepared with higher w/c i.e., 0.55 showed higher chloride binding capacity as compared to that prepared with lower w/c i.e., 0.45 irrespective of cement type, presence and type of corrosion inhibitors, and cation type of chloride salt in the composite chloride-sulfate solutions (Fig. 7.25 and Fig. 7.26). This is attributed to the dominant effect of more amount of chloride ions in the concrete made with higher w/c, which might have resulted in higher extent of binding of chloride ions with the hydrated cement phases.

While comparing the effect of exposure solution, it is observed that the chloride binding capacity of concrete exposed to composite chloride-sulfate solutions was lower as compared to that exposed to only chloride solutions irrespective of cement type, w/c, presence and type of corrosion inhibitors, and cation type of chloride salt in the exposure solutions (Fig. 7.23 to Fig. 7.26). The lower chloride binding in case of exposure to composite chloride-sulfate solutions may be attributed to the dominant effect of lower extent of physical binding of chloride ions with C-S-H due to conversion of C-S-H into non-cementitious M-S-H (magnesium silicate hydrate) in the presence of magnesium

sulfate in the concrete exposed to composite chloride-sulfate (NaCl or MgCl_2 or CaCl_2 plus MgSO_4) solutions.

7.5 Microstructure study

7.5.1 X-ray diffraction (XRD) analysis

As already stated in Chapter 3, to identify the phase composition of OPC and PPC concrete mixes prepared with and without corrosion inhibitors, and subjected to chloride and composite chloride-sulfate exposure solutions, XRD analysis was conducted on concrete powder samples collected from different depth intervals of cube specimens. The different phases present in the concrete mixes as observed from the obtained XRD patterns are calcium hydroxide (CH, peaks at $34.1^\circ 2\theta$, $36.6^\circ 2\theta$, and $47.2^\circ 2\theta$), calcium chloroaluminate (CCA, peaks at $11.2^\circ 2\theta$ and $23.2^\circ 2\theta$), and ettringite (E, peaks at $8.8^\circ 2\theta$ and $25.6^\circ 2\theta$). Further, the peaks in the XRD patterns of OPC as well as PPC concrete mixes at $20.8^\circ 2\theta$, $26.64^\circ 2\theta$, $39.45^\circ 2\theta$, $42.45^\circ 2\theta$, $45.5^\circ 2\theta$, and $50.2^\circ 2\theta$ are associated with quartz (Q), which is due to the presence of aggregates in the concrete. The peaks of feldspar (F) at $27.5^\circ 2\theta$ and that of calcium carbonate (CCB) at $29.4^\circ 2\theta$ were observed in OPC as well as in PPC concrete mixes irrespective of w/c, presence and type of corrosion inhibitors, and cation type of chloride salt in chloride and composite chloride-sulfate exposure solutions.

As mentioned in Chapter 3, from the obtained XRD patterns, the weight (%) of compounds namely ettringite (E), calcium chloroaluminate (CCA), calcium hydroxide (CH), calcium carbonate (CCB), and quartz (Q) were estimated from semi-quantification analysis using reference intensity ratio (RIR) matrix-flushing method. From the obtained results of XRD analysis, the variations in the formation of different compounds with cation type of chloride salt and exposure solution, cement type, w/c, corrosion inhibitor, and depth from exposure surface of concrete were analyzed using the peak intensity and weight (%) of the compounds.

7.5.1.1 Effect of cation type of chloride salt, and exposure solution on phase composition of concrete exposed to chloride and composite chloride-sulfate solutions

Typical XRD patterns showing the phase compositions of concrete mixes prepared from OPC and PPC; admixed with and without corrosion inhibitors; and exposed to different chloride and composite chloride-sulfate solutions are shown in Fig. 7.27 to Fig. 7.38. The remaining XRD patterns of concrete mixes prepared from OPC, and PPC are presented in Appendix B: Fig. B31 to Fig. B36. The XRD patterns shown in Fig. 7.27 to Fig. 7.38 and

Appendix B: Fig. B31 to Fig. B36 correspond to the concrete powder samples obtained from the depth interval of 5-10 mm from the exposure surface of concrete at the end of exposure period; and for chloride solutions of 3.5% NaCl, 3.5% MgCl₂, 3.5% CaCl₂, and composite chloride-sulfate solutions of 3.5% NaCl+3.5% MgSO₄, 3.5% MgCl₂+3.5% MgSO₄, and 3.5% CaCl₂+3.5% MgSO₄. Further, the plots of weight (%) of different compounds of concrete obtained from semi-quantification analysis using reference intensity ratio (RIR) matrix-flushing method are shown in Fig. 7.39 to Fig. 7.42 for concrete exposed to chloride solutions, and in Fig. 7.43, and Fig. 7.44 for concrete exposed to composite chloride-sulfate solutions. While evaluating the effect of chloride and composite chloride-sulfate solutions on microstructure of concrete, the XRD patterns shown in Fig. 7.46 to Fig. 7.51 (provided afterward) and that shown in Appendix B: Fig. B45 to Fig. B56 for different depth intervals from the exposure surface (discussed later) of concrete are also taken into consideration.

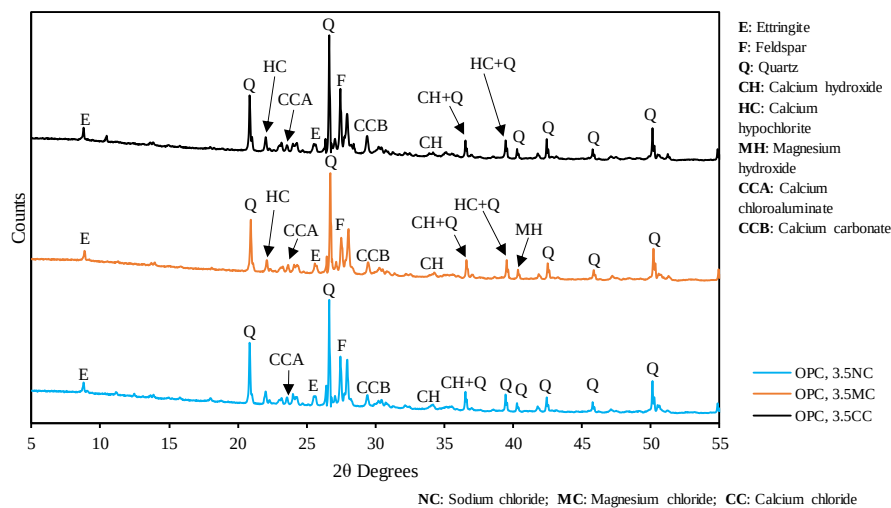


Fig. 7.27 XRD patterns of control concrete made from OPC at w/c of 0.45, and exposed to different chloride salt solutions

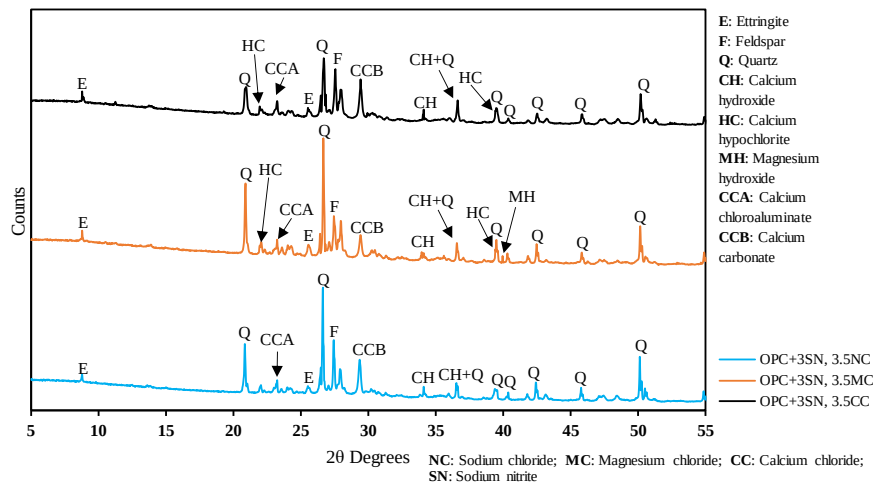


Fig. 7.28 XRD patterns of OPC concrete containing 3% NaNO_2 at w/c of 0.55, and exposed to different chloride salt solutions

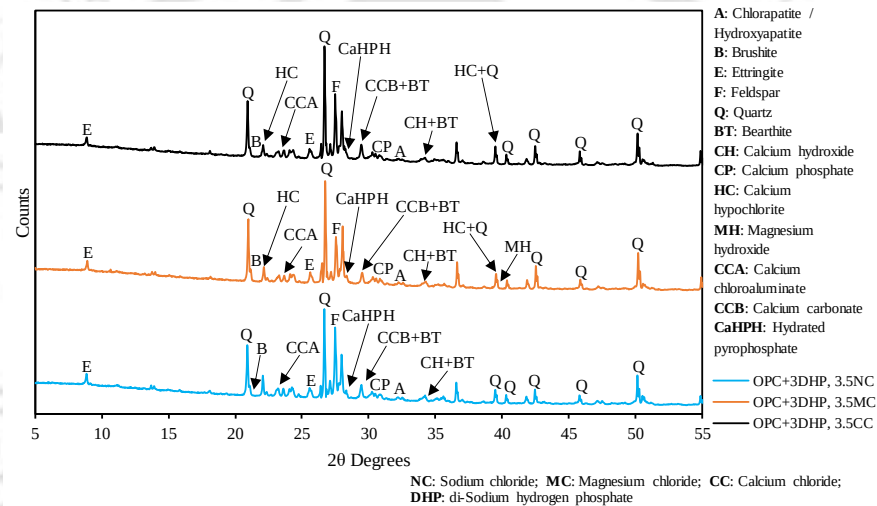


Fig. 7.29 XRD patterns of OPC concrete containing 3% DHP at w/c of 0.45, and exposed to different chloride salt solutions

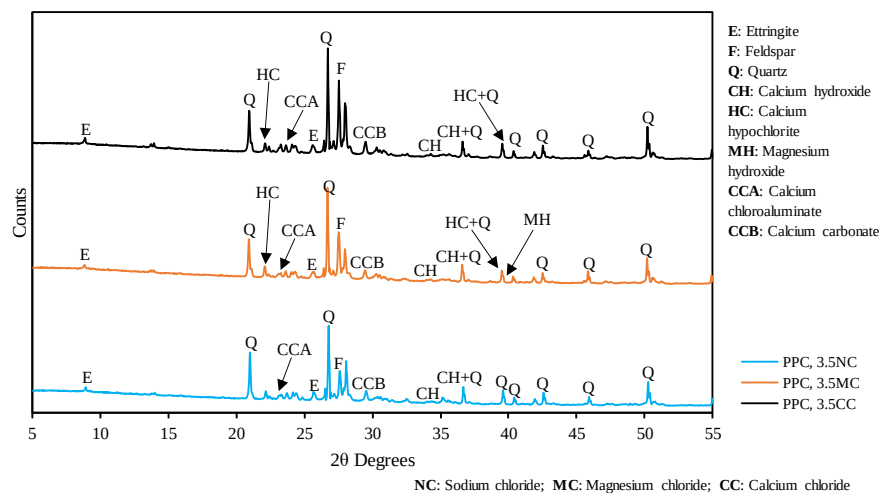


Fig. 7.30 XRD patterns of control concrete made from PPC at w/c of 0.45, and exposed to different chloride salt solutions

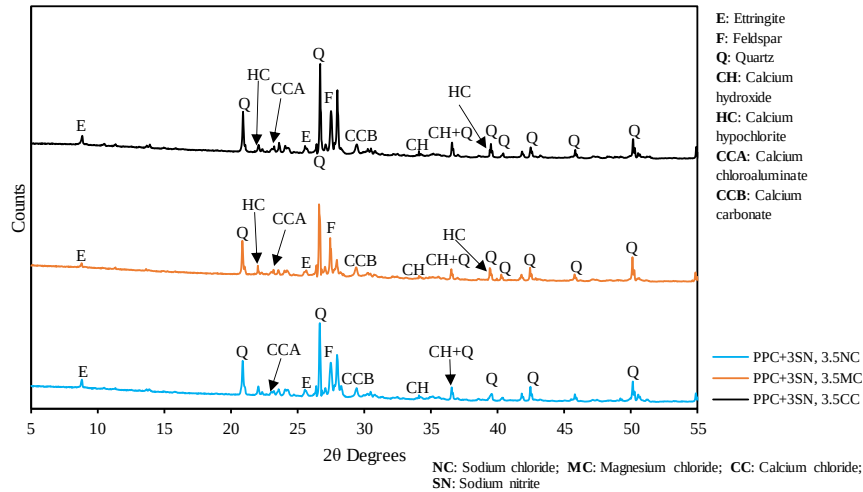


Fig. 7.31 XRD patterns of PPC concrete containing 3% NaNO₂ at w/c of 0.55, and exposed to different chloride salt solutions

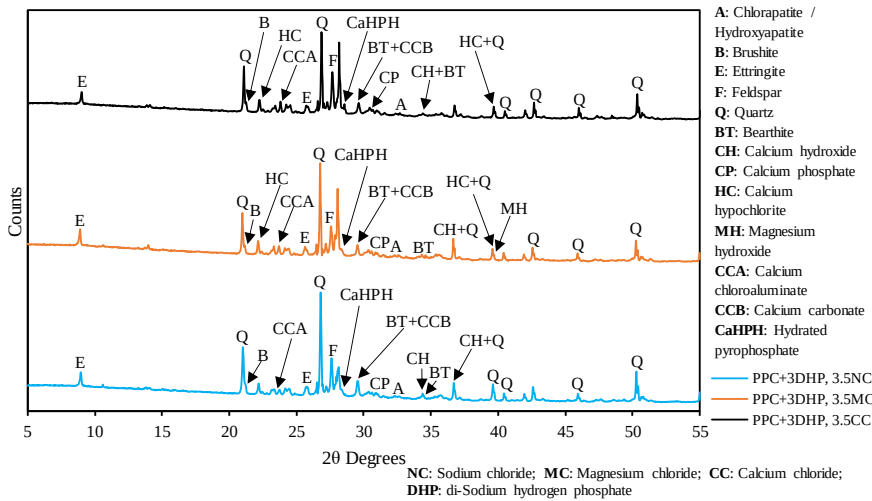


Fig. 7.32 XRD patterns of PPC concrete containing 3% DHP at w/c of 0.45, and exposed to different chloride salt solutions

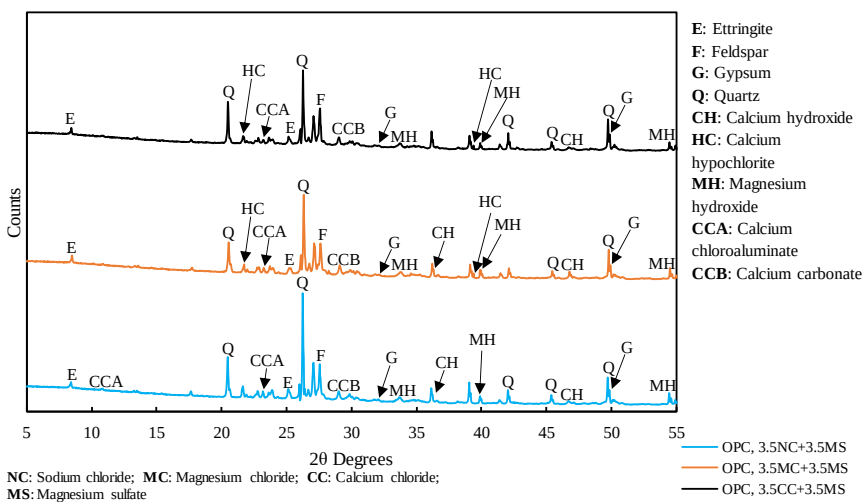


Fig. 7.33 XRD patterns of control concrete made from OPC at w/c of 0.55, and exposed to different composite chloride-sulfate solutions

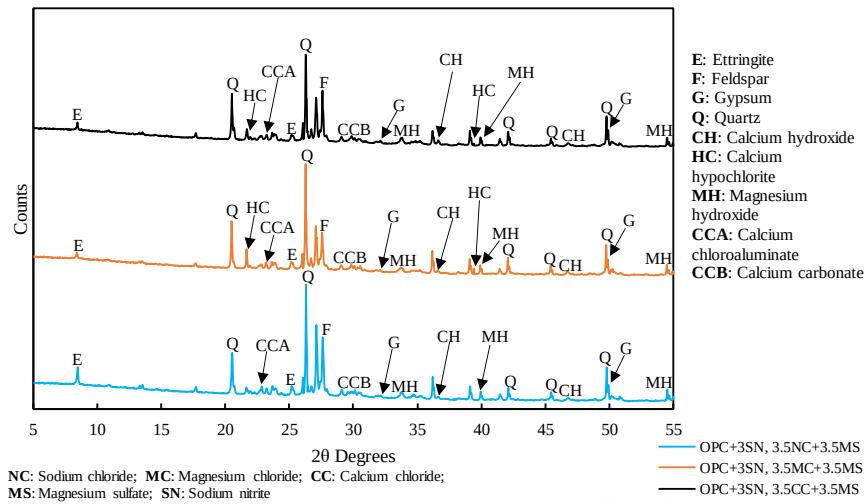


Fig. 7.34 XRD patterns of OPC concrete containing 3% NaNO_2 at w/c of 0.55, and exposed to different composite chloride-sulfate solutions

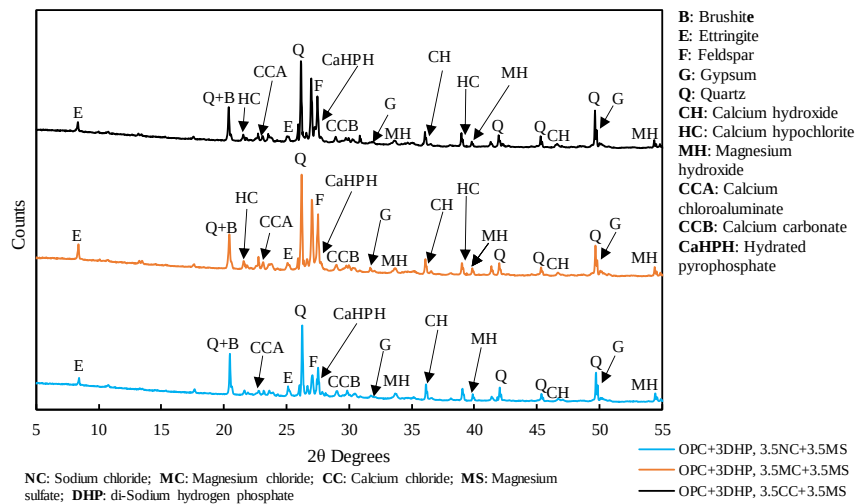


Fig. 7.35 XRD patterns of OPC concrete containing 3% DHP at w/c of 0.55, and exposed to different composite chloride-sulfate solutions

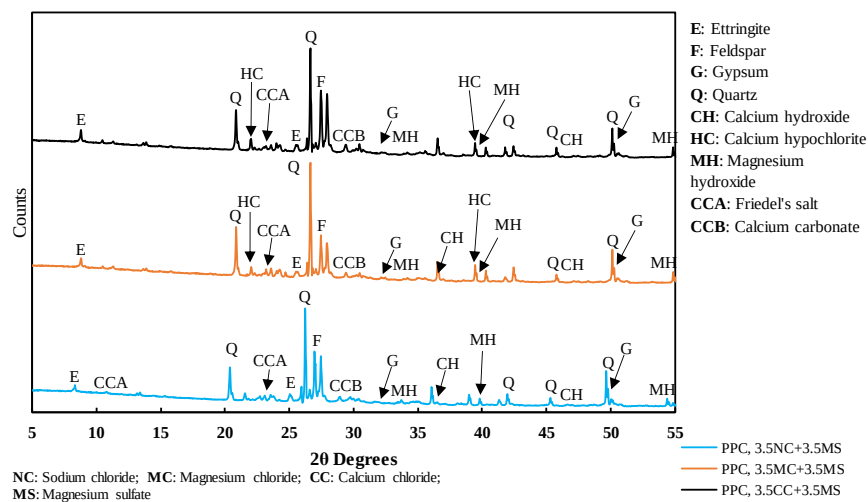


Fig. 7.36 XRD patterns of control concrete made from PPC at w/c of 0.55, and exposed to different composite chloride-sulfate solutions

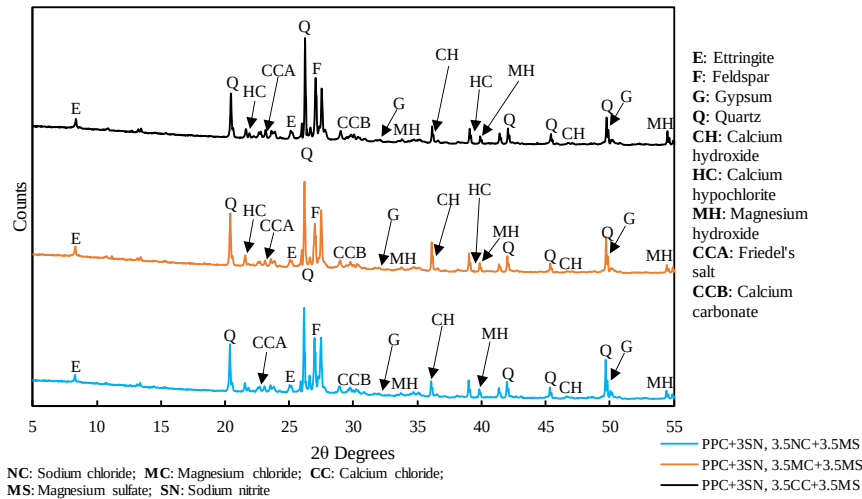


Fig. 7.37 XRD patterns of PPC concrete containing 3% NaNO_2 at w/c of 0.55, and exposed to different composite chloride-sulfate solutions

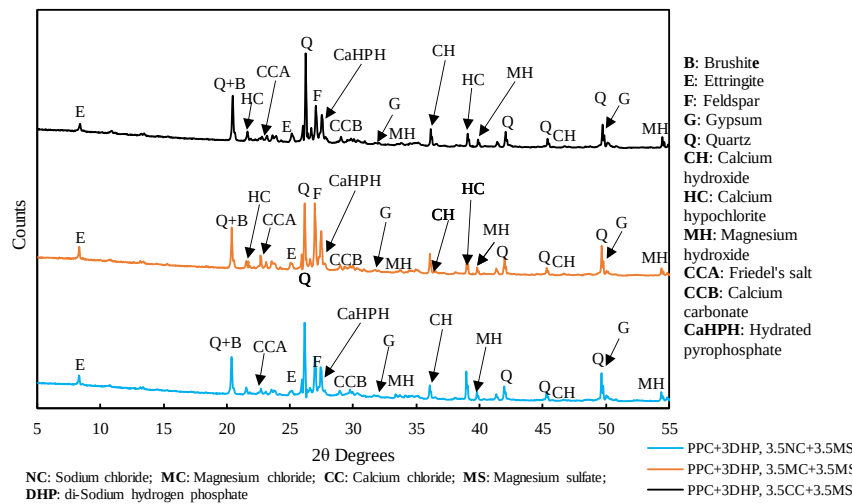
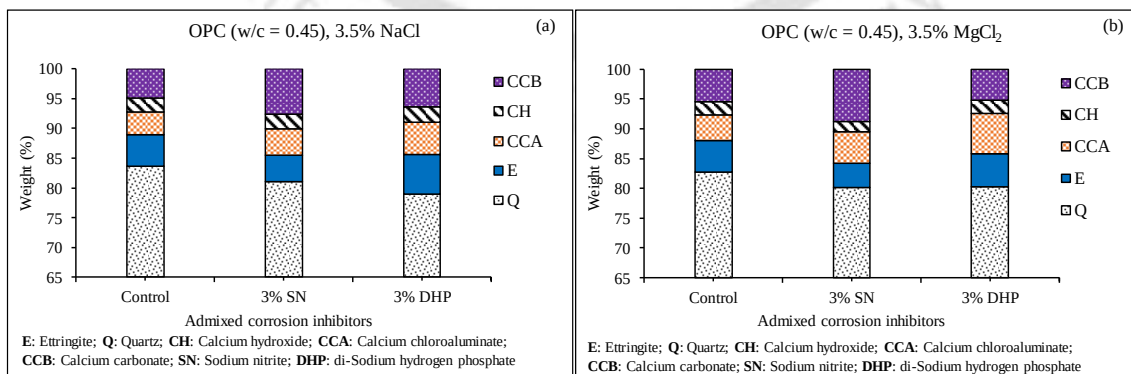


Fig. 7.38 XRD patterns of PPC concrete containing 3% DHP at w/c of 0.55, and exposed to different composite chloride-sulfate solutions



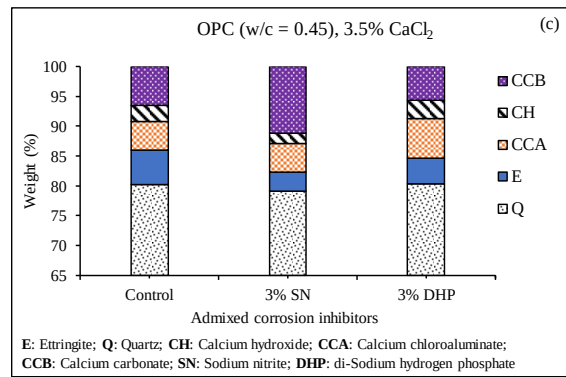


Fig. 7.39 Weight (%) of compounds from XRD patterns of OPC concrete admixed with, and without corrosion inhibitors at w/c of 0.45, and exposed to chloride salt solutions: (a) 3.5% NaCl solution, (b) 3.5% MgCl₂ solution, and (c) 3.5% CaCl₂ solution

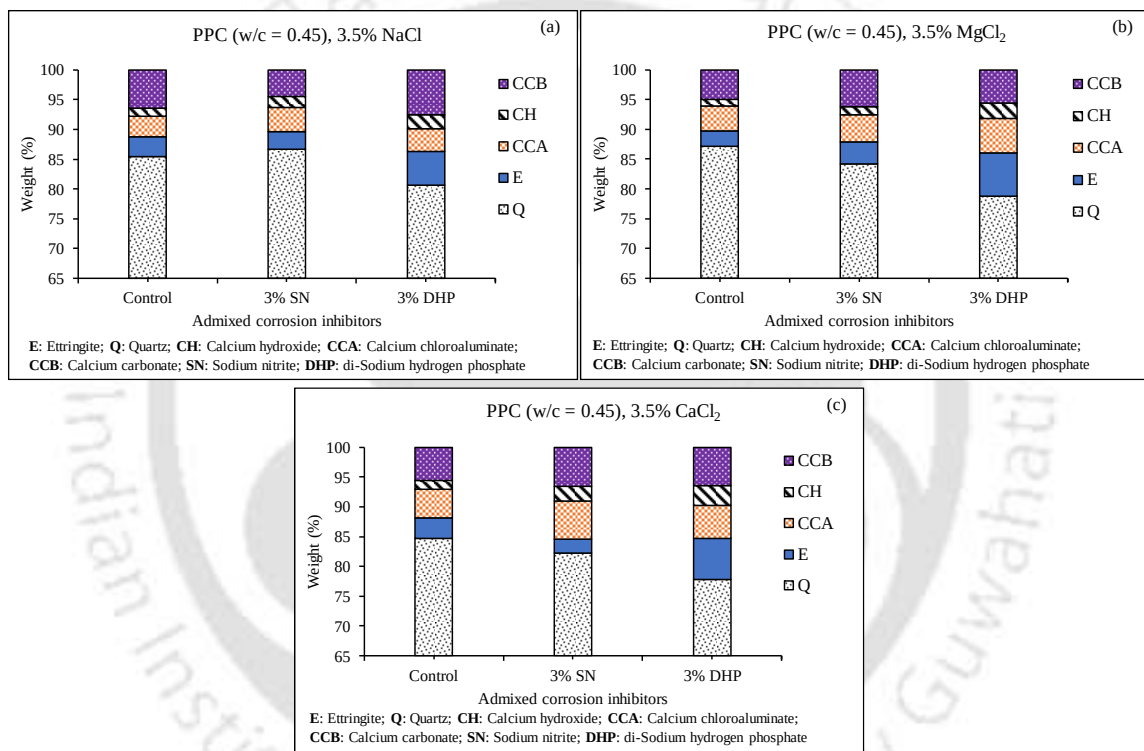
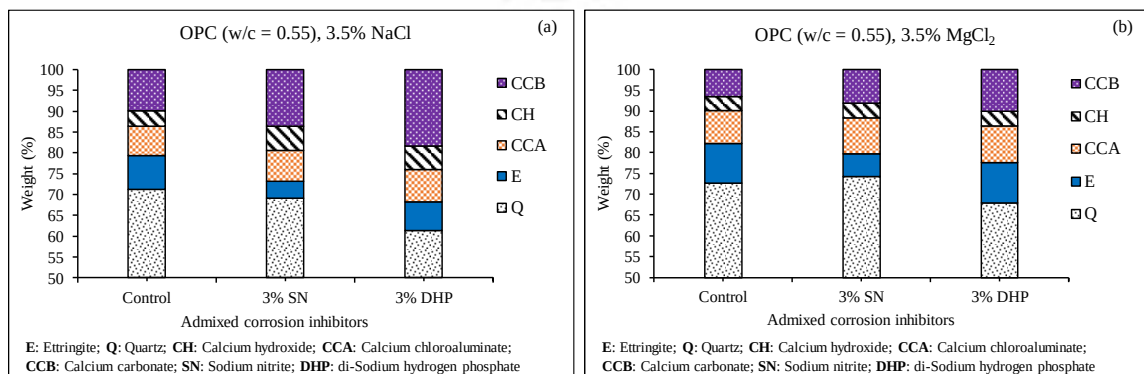


Fig. 7.40 Weight (%) of compounds from XRD patterns of PPC concrete admixed with, and without corrosion inhibitors at w/c of 0.45, and exposed to chloride salt solutions: (a) 3.5% NaCl solution, (b) 3.5% MgCl₂ solution, and (c) 3.5% CaCl₂ solution



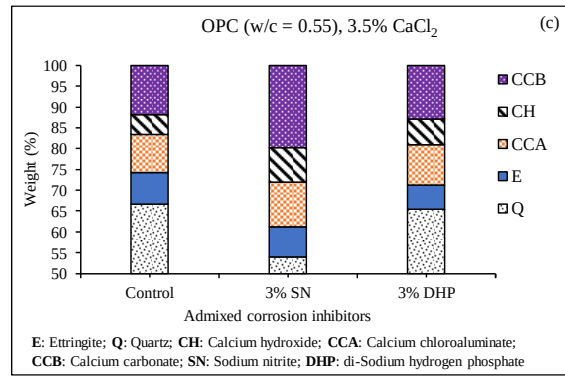


Fig. 7.41 Weight (%) of compounds from XRD patterns of OPC concrete admixed with, and without corrosion inhibitors at w/c of 0.55, and exposed to chloride salt solutions: (a) 3.5% NaCl solution, (b) 3.5% MgCl₂ solution, and (c) 3.5% CaCl₂ solution

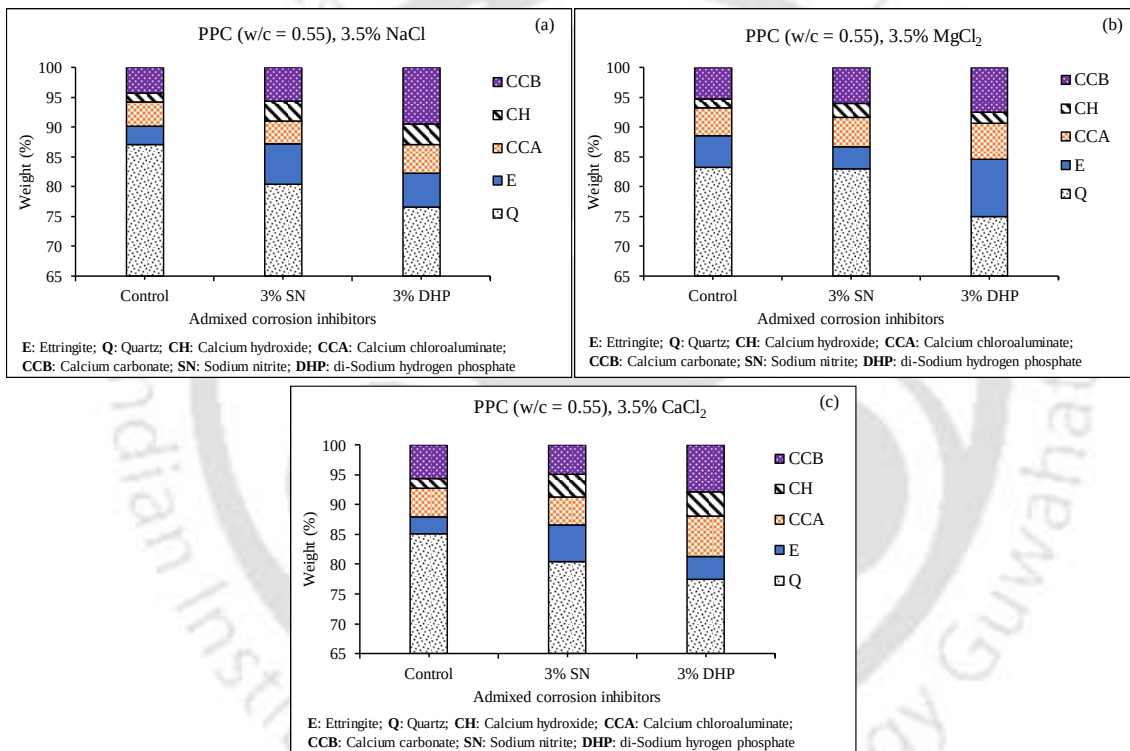
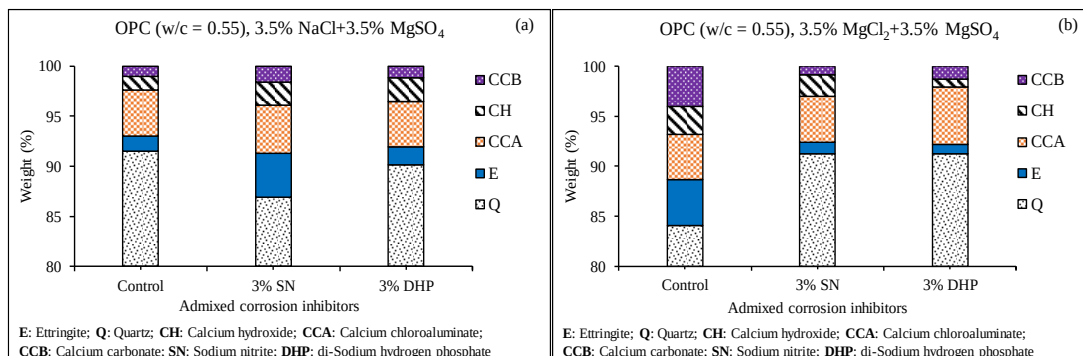


Fig. 7.42 Weight (%) of compounds from XRD patterns of PPC concrete admixed with, and without corrosion inhibitors at w/c of 0.55, and exposed to chloride salt solutions: (a) 3.5% NaCl solution, (b) 3.5% MgCl₂ solution, and (c) 3.5% CaCl₂ solution



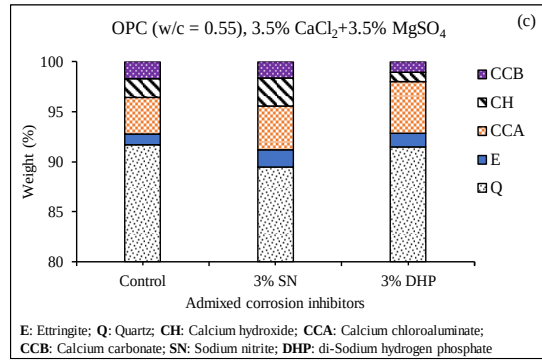


Fig. 7.43 Weight (%) of compounds from XRD patterns of OPC concrete admixed with, and without corrosion inhibitors at w/c of 0.55, and exposed to composite chloride-sulfate solutions: (a) 3.5% NaCl +3.5% MgSO_4 solution, (b) 3.5% MgCl_2 +3.5% MgSO_4 solution, and (c) 3.5% CaCl_2 +3.5% MgSO_4 solution

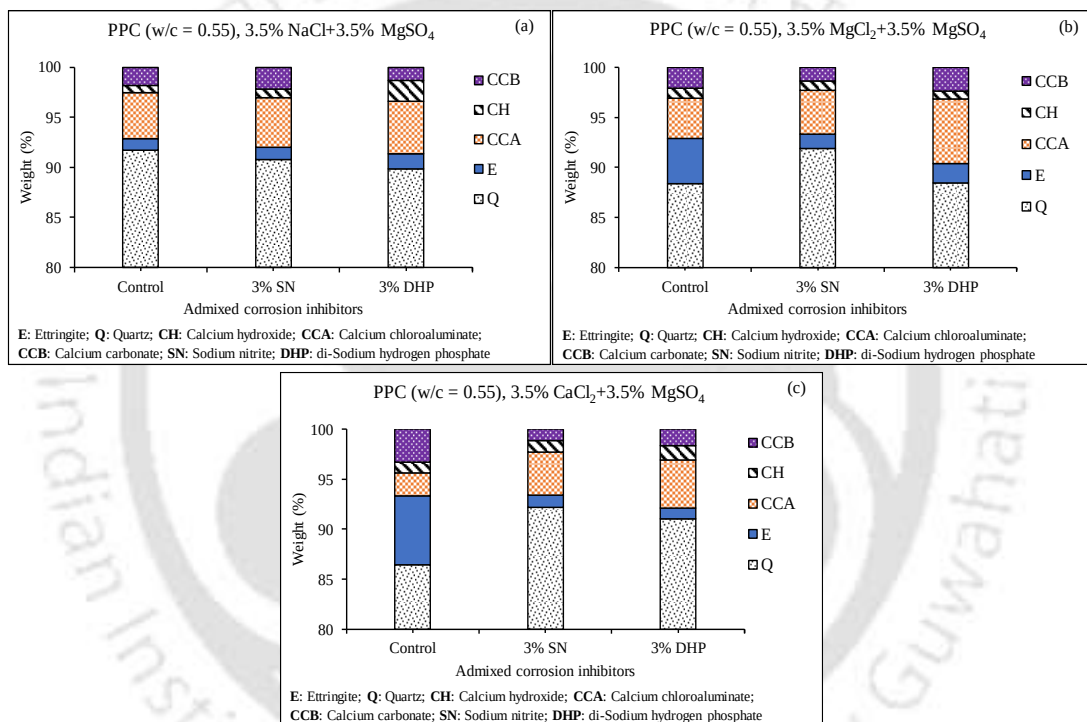


Fig. 7.44 Weight (%) of compounds from XRD patterns of PPC concrete admixed with, and without corrosion inhibitors at w/c of 0.55, and exposed to composite chloride-sulfate solutions: (a) 3.5% NaCl +3.5% MgSO_4 solution, (b) 3.5% MgCl_2 +3.5% MgSO_4 solution, and (c) 3.5% CaCl_2 +3.5% MgSO_4 solution

From Fig. 7.39 to Fig. 7.42, in case of exposure to chloride salt solutions, the weight (%) of calcium hydroxide (CH) obtained from XRD analysis was more in the concrete exposed to CaCl_2 solution as compared to that exposed to NaCl solution followed by MgCl_2 solution for both OPC and PPC at all depth intervals for control concrete (without corrosion inhibitors) and those admixed with corrosion inhibitors. The higher calcium hydroxide content in the concrete exposed to CaCl_2 solution as compared to NaCl and MgCl_2 solutions may be due to the effect of reaction of Ca^{2+} ions from CaCl_2 with $(\text{OH})^-$ ions present in the

concrete pore solution that results in precipitation of additional calcium hydroxide (Ca(OH)_2) [56]. Although, the consumption of Ca(OH)_2 in the formation of calcium hypochlorite (HC) reduces its amount in the concrete exposed to CaCl_2 solution, the formation of additional Ca(OH)_2 may be dominant over its consumption during the formation of calcium hypochlorite. The lower Ca(OH)_2 content in the concrete exposed to MgCl_2 solution as compared to that exposed to NaCl and CaCl_2 solutions is attributed to the consumption of Ca(OH)_2 in the formation of calcium hypochlorite (HC), and conversion of Ca(OH)_2 to Mg(OH)_2 in presence of MgCl_2 [56]. The formation of Mg(OH)_2 in the concrete exposed to MgCl_2 solution is confirmed by its peaks observed at $39.92^\circ 2\theta$ in the XRD patterns for both OPC and PPC concrete irrespective of w/c and presence of corrosion inhibitors as noted from Fig. 7.27 to Fig. 7.32, and Appendix B: Fig. B31 to Fig. B36. In OPC and PPC concrete mixes admixed with or without corrosion inhibitors and exposed to MgCl_2 and CaCl_2 solutions, the peaks of calcium hypochlorite (HC) are observed at $21.7^\circ 2\theta$ and $39.4^\circ 2\theta$ in the XRD patterns as shown in Fig. 7.27 to Fig. 7.32, and Appendix B: Fig. B31 to Fig. B36. As already stated in Chapter 4, in the presence of water, CaCl_2 reacts with Ca(OH)_2 and forms calcium hypochlorite in the concrete exposed to CaCl_2 solution [52]. In case of concrete exposed to MgCl_2 solution, the reaction of MgCl_2 with Ca(OH)_2 leads to the formation of Mg(OH)_2 and CaCl_2 . In the presence of water, CaCl_2 further reacts with Ca(OH)_2 and produces calcium hypochlorite [52]. The peak intensity of calcium hypochlorite is more in the concrete exposed to MgCl_2 solution as compared to that exposed to CaCl_2 solution (Fig. 7.27 to Fig. 7.32, and Appendix B: Fig. B31 to Fig. B36) thereby indicating its formation in higher amount in the concrete exposed to MgCl_2 solution than CaCl_2 solution.

In case of exposure to composite chloride-sulfate solutions, for both OPC and PPC, there was no systematic variation in weight (%) of calcium hydroxide (obtained from XRD analysis) among cation type of chloride salt in the exposure solution for control concrete as well as that admixed with corrosion inhibitors as evident from Fig. 7.43 and Fig. 7.44. The formation of magnesium hydroxide (Mg(OH)_2) and the effect of alterations in the extent of leaching of calcium hydroxide in the presence of chloride ions might have resulted in the unsystematic variation in the amount of calcium hydroxide in the concrete exposed to composite chloride-sulfate solutions. While comparing chloride and composite chloride-sulfate solutions, the weight (%) of calcium hydroxide was lower in the concrete exposed to composite chloride-sulfate solutions as compared to that exposed to only chloride

solutions irrespective of cement type, presence and type of corrosion inhibitor, and type of chloride salt in the exposure solutions (Fig. 7.39 to Fig. 7.44). The lower calcium hydroxide content in the concrete exposed to composite chloride-sulfate solutions may be due to the dominant effect of its consumption in the formation of magnesium hydroxide (brucite). The formation of magnesium hydroxide (MH) in the concrete exposed to composite chloride-sulfate solutions is confirmed by its peaks observed at $39.92^\circ 2\theta$ in the XRD patterns for both OPC and PPC concrete irrespective of presence and type of corrosion inhibitors, and type of chloride salt in the exposure solutions as observed from Fig. 7.33 to Fig. 7.38. Further, the formation of magnesium hydroxide (MH) was higher in the concrete exposed to $\text{MgCl}_2 + \text{MgSO}_4$ solution as compared to that exposed to only MgCl_2 solution. The peak intensity of magnesium hydroxide ($\text{Mg}(\text{OH})_2$) in the XRD patterns as observed from Fig. 7.33 to Fig. 7.38 indicated its formation in higher amount in the concrete exposed to $\text{MgCl}_2 + \text{MgSO}_4$ solution as compared to $\text{NaCl} + \text{MgSO}_4$ solution followed by $\text{CaCl}_2 + \text{MgSO}_4$ solution for both OPC and PPC in control concrete and that admixed with corrosion inhibitors. The more formation of $\text{Mg}(\text{OH})_2$ in the concrete exposed to $\text{MgCl}_2 + \text{MgSO}_4$ solution may be due to the availability of more concentration of Mg^{2+} ions in the concrete, which might have resulted in conversion of $\text{Ca}(\text{OH})_2$ to $\text{Mg}(\text{OH})_2$ to a comparatively higher extent. In Fig. 7.33 to Fig. 7.38, the presence of calcium hypochlorite is identified through its peaks at $21.7^\circ 2\theta$, and $39.4^\circ 2\theta$ in the XRD patterns of concrete exposed to $\text{MgCl}_2 + \text{MgSO}_4$, and $\text{CaCl}_2 + \text{MgSO}_4$ solutions. The peak intensity of calcium hypochlorite was comparatively higher in case of exposure to $\text{MgCl}_2 + \text{MgSO}_4$ solution as compared to $\text{CaCl}_2 + \text{MgSO}_4$ solution.

In case of exposure to chloride solutions, the formation of calcium chloroaluminate (CCA) was more in the concrete exposed to CaCl_2 solution as compared to MgCl_2 solution followed by NaCl solution at all depth intervals for both cements in control concrete as well as that admixed with corrosion inhibitors as observed from the weight (%) of CCA obtained from the XRD analysis (Fig. 7.39 to Fig. 7.42). As stated earlier in Chapter 6, the higher calcium chloroaluminate content in the concrete exposed to CaCl_2 solution as compared to MgCl_2 solution may be ascribed to the reaction of chloride ions with C_3A to a comparatively higher extent when the chloride ions are associated with calcium cation. The lower calcium chloroaluminate content in the concrete exposed to NaCl solution in comparison to that exposed to MgCl_2 and CaCl_2 solutions may be ascribed to the effect of higher pH of electrolytic pore solution of concrete in the presence of NaCl , which increases the solubility

of calcium chloroaluminate (CCA) [52]. In case of exposure to composite chloride-sulfate solutions, the weight (%) of calcium chloroaluminate (CCA) obtained from XRD analysis was mostly higher in the concrete exposed to NaCl+MgSO₄ solution as compared to MgCl₂+MgSO₄ solution followed by CaCl₂+MgSO₄ solution for both cements irrespective of presence and type of corrosion inhibitors. The reason for this variation in formation of calcium chloroaluminate with cation type of chloride salt in the composite chloride-sulfate solutions was already explained in Section 6.3 and 6.4.1 (Chapter 6). From the weight (%) of calcium chloroaluminate (CCA) shown in Fig. 7.39 to Fig. 7.44, it is observed that in case of OPC, the formation of CCA was higher in the concrete exposed to chloride solutions than that exposed to composite chloride-sulfate solutions, whereas in case of PPC, the opposite variation in formation of CCA was observed between chloride and composite chloride-sulfate solutions irrespective of presence of corrosion inhibitors, and type of chloride salt in the exposure solutions. In OPC concrete, the more formation of calcium chloroaluminate in case exposure to chloride solutions may be attributed to the effect of reaction of chloride ions with C₃A to a higher extent as compared that in case of exposure to composite chloride-sulfate solutions. In PPC concrete, the higher calcium chloroaluminate (CCA) content in case of exposure to composite chloride-sulfate solutions can be ascribed to the dominant effect of lower extent of conversion of CCA to ettringite in the presence of sulfate ions.

From Fig. 7.39 to Fig. 7.44, it is observed that there was no systematic variation in weight (%) of ettringite (obtained from XRD analysis) with cation type of chloride salt in chloride as well as composite chloride-sulfate solutions irrespective of cement type, and presence of corrosion inhibitors. Besides, the amount of ettringite was mostly lower in the concrete exposed to composite chloride-sulfate solutions as compared to that exposed to only chloride solutions for both cements, corrosion inhibitors and chloride salts in the exposure solutions. In case of exposure to composite chloride-sulfate solutions, the reaction of sulfate ions with C₃A results in the formation of ettringite in concrete. The lower amount of ettringite in the concrete exposed to composite chloride-sulfate solutions may be attributed to the dominant effect of lower pH of concrete in the presence of magnesium sulfate that might have resulted in decomposition of ettringite [200, 201] to a higher extent.

In the concrete exposed to composite chloride-sulfate solutions, the peaks of gypsum (G) were observed at 32.1° 2θ, and 50.5° 2θ in the XRD patterns shown in Fig. 7.33 to Fig. 7.38, irrespective of cement type, presence and type of corrosion inhibitors, and type of

chloride salt in the composite chloride-sulfate solutions. From the obtained XRD patterns, the variation in peak intensity of gypsum was not systematic with cation type associated with chloride ions in the composite chloride-sulfate solutions. As already stated in Chapter 6 (Section 6.4.1), this may be attributed to the dominant effect of alterations in the extent of reaction of sulfate ions with calcium hydroxide in the combined presence of chloride ions associated with different types of cation.

Typical plots showing the weight (%) of compounds obtained from the XRD patterns of concrete mixes at w/c of 0.55, and exposed to chloride solutions of different concentrations i.e., 1.5%, 3.5%, and 5.5% for each chloride salt (NaCl, MgCl₂, and CaCl₂) are shown in Fig. 7.45. The remaining figures are presented in Appendix B: Fig. B37 to Fig. B44. It may be noted that the weight (%) of the compounds obtained from the XRD patterns correspond to the concrete powder samples collected from the depth interval of 5-10 mm from the exposure surface of cube specimens.

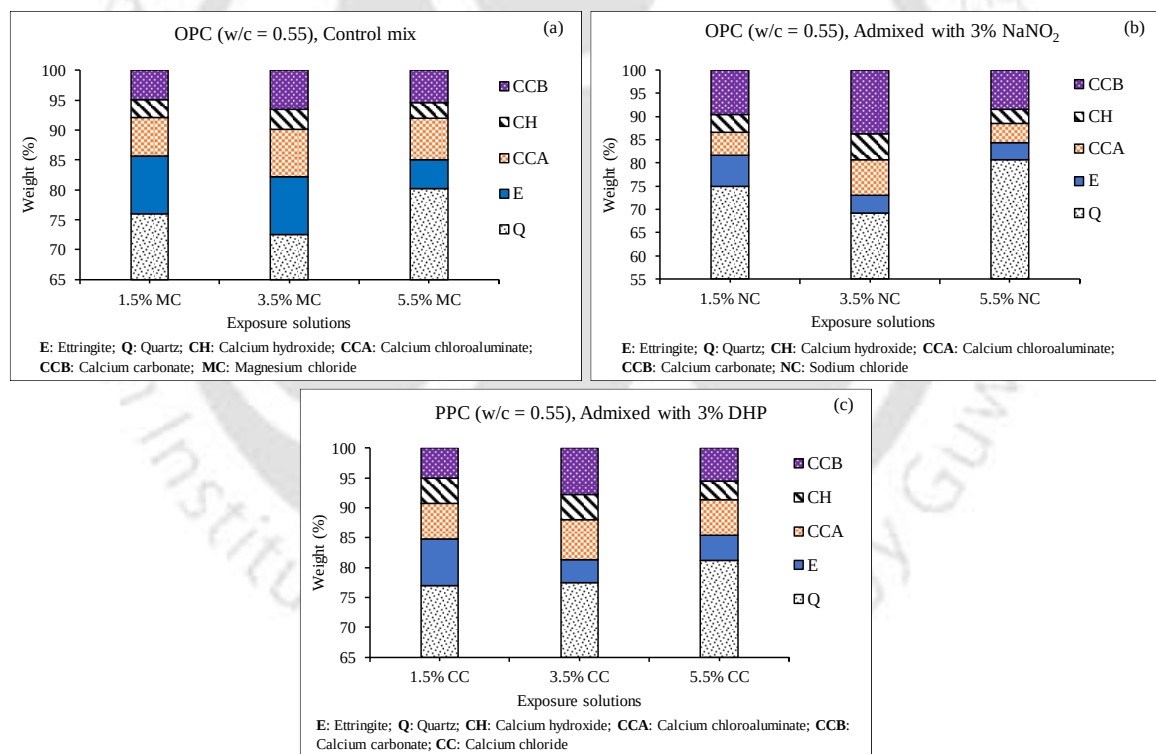


Fig. 7.45 Weight (%) of compounds from XRD patterns of concrete exposed to chloride solutions of different concentrations (1.5%, 3.5%, and 5.5%): (a) control mix exposed to MgCl₂ solution, (b) concrete admixed with 3% NaNO₂, exposed to NaCl solution and, (c) concrete admixed with 3% DHP, exposed to CaCl₂ solution

From Fig. 7.45 and Appendix B: Fig. B43 and Fig. B44, it is observed that the weight (%) of calcium hydroxide (CH) mostly decreased with increase in concentration of chloride salt in the exposure solution irrespective of cation type chloride salt, cement type, and presence

of corrosion inhibitors. The lower amount of calcium hydroxide in the concrete exposed to chloride salt solutions of higher concentration may be attributed to the leaching of calcium hydroxide in the presence of chloride ions to a higher extent due to presence of more amount of chloride ions in the concrete exposed to chloride solutions of higher concentration [202, 203]. It may be noted that the free chloride content was higher in the concrete exposed to chloride solution of higher concentration as compared to that exposed to chloride solution of lower concentration (discussed earlier in Section 7.3.1). The weight (%) of calcium chloroaluminate was mostly higher in the concrete exposed to 3.5% chloride salt solution than that exposed to 5.5% chloride salt solution followed by 1.5% chloride salt solution as evident from Fig. 7.45 and Appendix B: Fig. B43 and Fig. B44. As already discussed in Section 7.4, this may be due to the effect of binding of chloride ions with available C_3A to a comparatively greater extent in case of exposure to chloride solutions with 3.5% chloride salt concentration as compared to chloride salt concentrations of 5.5% and 1.5%. With increase in concentration of chloride salt in the exposure solutions, the weight (%) of ettringite in concrete mostly decreased as evident from Fig. 7.45 and Appendix B: Fig. B43 and Fig. B44. The reason behind this may be the solubility of ettringite to a greater extent in the presence of higher amount of chloride ions in the concrete exposed to chloride solutions of higher concentration.

7.5.1.2 Effect of corrosion inhibitors on phase composition of concrete exposed to chloride and composite chloride-sulfate solutions

From Fig. 7.39 to Fig. 7.44, it is observed that the weight (%) of calcium hydroxide (obtained from XRD analysis) was mostly higher in the concrete mix admixed with corrosion inhibitors as compared to control concrete mix (without corrosion inhibitor) irrespective of cement type, w/c, and cation type of chloride salt in chloride, and composite chloride-sulfate exposure solutions. As already stated in Chapter 6 (Section 6.4.1), the lower amount of calcium hydroxide in control concrete mix may be due to the effect of its leaching to a comparatively higher extent in the presence of more amount of chloride ions. It may be noted that the amount of free chloride was higher in control concrete due to more ingress of chloride ions as compared to that in the concrete admixed with corrosion inhibitors (Fig. 7.1 to Fig. 7.10 and Appendix B: Fig. B1 to Fig. B6).

While comparing between corrosion inhibitors, it is observed that the concrete admixed with DHP mostly showed higher weight (%) of calcium hydroxide (obtained from XRD analysis) as compared to that admixed with $NaNO_2$ irrespective of cement type, w/c, and

cation type of chloride salt in chloride exposure solutions as observed from Fig. 7.39 to Fig. 7.42. Although, calcium hydroxide (CH) was consumed in the formation of phosphate based compounds such as calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), chlorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{Cl}$), and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) [128, 189] in the concrete admixed with DHP, the leaching of calcium hydroxide to a comparatively higher extent due to presence of more amount of chloride ions in the concrete admixed with NaNO_2 might have resulted in lower amount of calcium hydroxide as compared to that admixed with DHP. As stated earlier, the free chloride ion content was higher in the concrete admixed with NaNO_2 than that admixed with DHP (Fig. 7.3 to Fig. 7.6). In case of exposure to composite chloride-sulfate solutions, the concrete admixed with NaNO_2 mostly showed higher amount of calcium hydroxide (CH) as compared to that admixed with DHP irrespective of cement type and cation type of chloride salt in composite chloride-sulfate solutions as observed from the weight (%) of calcium hydroxide shown in Fig. 7.43 and 7.44. The lower amount of calcium hydroxide (CH) in the concrete admixed with DHP as compared to NaNO_2 may be due to leaching of calcium hydroxide to a greater extent in the presence of higher amount of chloride ions as well as consumption of calcium hydroxide in the formation of phosphate based compounds in the concrete containing DHP. It may be noted that in case of exposure to composite chloride-sulfate solutions, the free chloride ion content was higher in the concrete admixed with DHP as compared to that admixed with NaNO_2 (Fig. 7.7 (b, c), Fig. 7.8 (b, c), Fig. 7.9 (b, c), and Fig. 7.10 (b, c)).

From Fig. 7.39 to Fig. 7.44, it is observed that the weight (%) of calcium chloroaluminate (Friedel's salt) obtained from XRD analysis is mostly higher in the concrete admixed with corrosion inhibitors as compared to control concrete irrespective of cement type, w/c, and cation type of chloride salt in chloride, and composite chloride-sulfate solutions. This is attributed to the effect of reaction of chloride ions with C_3A to a comparatively greater extent in the presence of corrosion inhibitors thereby lowering the free chloride ion content in the concrete admixed with corrosion inhibitors. Further, the formation of calcium chloroaluminate (CCA) is mostly higher in the concrete admixed with DHP as compared to that admixed with NaNO_2 in case of exposure to chloride as well as composite chloride-sulfate solutions as evident from the weight (%) of CCA shown in Fig. 7.39 to Fig. 7.44. In case of concrete containing NaNO_2 , the chloride ions partially replace the NO_2^- ions in nitrite-AFm and form Friedel's salt. The higher weight (%) of Friedel's salt in the concrete

containing DHP as compared to that containing NaNO_2 is ascribed to the effect of phosphate ions that helps in the formation of Friedel's salt to a higher extent [105, 130].

From Fig. 7.39 to Fig. 7.44, it is observed that there was no systematic variation in weight (%) of ettringite (obtained from XRD analysis) between control concrete (without corrosion inhibitors) and those admixed with corrosion inhibitors irrespective of cement type, and cation type of chloride salt in chloride, and composite chloride-sulfate solutions. In case of exposure to chloride solutions, the weight (%) of ettringite (E) was mostly lower in the concrete admixed with NaNO_2 as compared to that admixed with DHP irrespective of cement type, w/c, and chloride salt in the exposure solutions. As already discussed in Section 6.4.1 (Chapter 6), in case of exposure to chloride solutions, the lower amount of ettringite in the concrete admixed NaNO_2 may be ascribed to the effect of solubility of ettringite in the presence of chloride ions to a higher extent as a result of penetration of more amount of chloride ions into the concrete admixed with NaNO_2 than that admixed with DHP. It may be noted that the free chloride content was higher in the concrete admixed with NaNO_2 than that admixed with DHP in case of exposure to chloride solutions (already discussed in Section 7.3.4). In case of exposure to composite chloride-sulfate solutions, the weight (%) of ettringite (E) obtained from XRD analysis was mostly higher in the concrete admixed with NaNO_2 as compared to that admixed with DHP irrespective of cement type, and chloride salt in the exposure solutions. The lower amount of ettringite in the concrete admixed with DHP is ascribed to higher solubility of ettringite in the presence of chloride due to more ingress of chloride ions into the concrete admixed with DHP than that admixed with NaNO_2 in case of exposure to composite chloride-sulfate solutions.

From Fig. 7.33 to Fig. 7.38, it is observed that the concrete admixed with corrosion inhibitors mostly showed higher peak intensity of gypsum (G) in the XRD patterns as compared to control concrete in case of exposure to composite chloride-sulfate solutions. The lower amount of calcium hydroxide in control concrete as compared to that admixed with corrosion inhibitors may be the reason for lower formation of gypsum in the presence of sulfate ions in control concrete than that admixed with corrosion inhibitors. Further, between NaNO_2 , and DHP, the peak intensity of gypsum in the XRD patterns was mostly higher in the concrete admixed with NaNO_2 as compared to that admixed with DHP irrespective of cement type, and chloride salt in the composite chloride-sulfate solutions as observed from Fig. 7.34, Fig. 7.35, Fig. 7.37, and Fig. 7.38. This may be due to lower availability of calcium hydroxide (as obtained from XRD analysis) in the concrete admixed

with DHP thereby resulting in lower formation of gypsum in the presence of sulfate as compared to that admixed with NaNO_2 in case of exposure to composite chloride-sulfate solutions.

In Fig. 7.29, Fig. 7.32, Fig. 7.35, Fig. 7.38, and Appendix B: Fig. B33 and B36, the peaks of hydrated pyrophosphate ($\text{Ca}_3\text{H}_2(\text{P}_2\text{O}_7)_2\text{H}_2\text{O}$) are observed at $28.4^\circ 2\theta$, and those of brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) are observed at $20.94^\circ 2\theta$ in the XRD patterns of concrete mixes admixed with DHP. In addition, the peaks of bearthite, which is a AFm (Pho)-like structure ($\text{Ca}_2\text{Al}(\text{PO}_4)_2\text{OH}$), at $29.2^\circ 2\theta$ and $34.9^\circ 2\theta$, calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) at $27.76^\circ 2\theta$ and $31.02^\circ 2\theta$, and chlorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{Cl}$)/ hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) at $32.29^\circ 2\theta$ are observed in the XRD patterns of concrete admixed with DHP for both OPC and PPC irrespective of w/c, and chloride salt in chloride, and composite chloride-sulfate solutions.

7.5.1.3 Effect of cement type on phase composition of concrete exposed to chloride and composite chloride-sulfate solutions

From Fig. 7.39 to Fig. 7.44, it is observed that the weight (%) of calcium hydroxide (CH) was higher in OPC concrete as compared to PPC concrete, which indicates the presence of higher amount of calcium hydroxide in OPC concrete mixes than PPC concrete mixes irrespective of presence of corrosion inhibitors, and type of chloride salt in chloride and composite chloride-sulfate solutions. The lower amount of calcium hydroxide in PPC concrete mixes as compared to OPC concrete mixes may be ascribed to its consumption in the pozzolanic reaction in PPC concrete. Further, the peak intensity of magnesium hydroxide (MH) was higher in OPC concrete than PPC concrete in case of exposure to MgCl_2 solution, and composite chloride-sulfate solutions regardless of presence of corrosion inhibitors (Fig. 7.27 to Fig. 7.38 and Appendix B: Fig. B31 to Fig. B36). This may be attributed to the conversion of calcium hydroxide to magnesium hydroxide in the presence of Mg^{2+} ions to a comparatively higher extent in OPC concrete due to more amount of calcium hydroxide in OPC concrete than that in PPC concrete.

Further, the weight (%) of calcium chloroaluminate (CCA) obtained from XRD analysis is more in OPC concrete mixes as compared to PPC concrete mixes irrespective of presence and type of corrosion inhibitors, and chloride salt in the exposure solutions i.e., both chloride and composite chloride-sulfate solutions. This indicates formation of more amount of calcium chloroaluminate in OPC concrete mixes as compared to PPC concrete mixes. This may be due to the presence of higher C_3A content in OPC concrete mixes as compared

to PPC concrete mixes thereby resulting in reaction of chloride ions with C_3A to a greater extent in OPC concrete mixes, and leading to higher chloride binding in OPC concrete than PPC concrete. As stated earlier in Section 7.4, the chloride binding capacity (R) of OPC concrete was higher as compared to PPC concrete in case of exposure to chloride as well as composite chloride-sulfate solutions.

From Fig. 7.39 to Fig. 7.44, it is observed that the weight (%) of ettringite (E) is mostly higher in OPC concrete as compared to PPC concrete thereby indicating formation of more amount of ettringite in the former as compared to that in the latter. Although, C_3A was consumed in the formation of higher amount of calcium chloroaluminate in OPC concrete (as discussed earlier), the availability of more C_3A content in OPC concrete resulted in formation of more amount of ettringite in OPC than that in PPC concrete.

The peak intensity of gypsum (G) was mostly higher in OPC concrete than PPC concrete irrespective of presence of corrosion inhibitors, and cation type of chloride salt in composite chloride-sulfate solutions as observed from the XRD patterns shown in Fig. 7.33 to Fig. 7.38. This may be attributed to the effect of reaction of sulfate ions with calcium hydroxide to a comparatively greater extent as a result of availability of higher amount of calcium hydroxide and ingress of more amount of sulfate ions into OPC concrete as compared to PPC concrete.

7.5.1.4 Effect of w/c on phase composition of concrete exposed to chloride solutions

While comparing the effect of w/c, it is observed from the results of XRD analysis that the weight (%) of calcium hydroxide (CH), calcium chloroaluminate (CCA), and ettringite (E) were mostly higher in the concrete made with w/c of 0.55 as compared to that made with w/c of 0.45 irrespective of cement type, presence of corrosion inhibitors and chloride salt in the chloride exposure solutions as evident from Fig. 7.39 to Fig. 7.44. It may be noted that the weight (%) of above compounds obtained from the XRD analysis correspond to the concrete powder samples collected from the depth interval of 5-10 mm from the exposure surface of cube specimens. The higher amount of calcium hydroxide at w/c of 0.55 may be due to the effect of its leaching in the presence of chloride ions to a lower extent as compared to that at w/c of 0.45. As discussed earlier in Section 7.3.2 and Section 7.3.4, the free chloride ion content was lower in the depth intervals of 0-5 mm and 5-10 mm i.e., till depth of 10 mm from the exposure surface of concrete made with w/c 0.55 as compared to that made with w/c of 0.45. The formation of more amount of calcium

chloroaluminate (CCA) at w/c of 0.55 is attributed to the reaction of chloride ions with hydrated C_3A to a comparatively higher extent as compared to that at w/c of 0.45. The reason behind higher amount of ettringite in the concrete made with w/c of 0.55 may be due to lower extent of solubility of ettringite in the presence of lower amount of chloride ions till the depth interval of 10 mm from exposure surface of concrete made with w/c of 0.55 as compared to w/c of 0.45.

7.5.1.5 Effect of depth from exposure surface on phase composition of concrete exposed to chloride solutions

Typical XRD patterns showing the phase compositions of concrete at different depth intervals from the exposure surface at w/c of 0.55 and exposed to different chloride solutions are shown in Fig. 7.46 to Fig. 7.48 for OPC and in Fig. 7.49 to Fig. 7.51 for PPC. The remaining figures are presented in Appendix B: Fig. B45 to Fig. B56. Further, the weight (%) of the compounds obtained from the XRD patterns using reference intensity ratio (RIR) matrix-flushing method are shown in Fig. 7.52 to Fig. 7.54 for OPC and, in Fig. 7.55 to Fig. 7.57 for PPC.

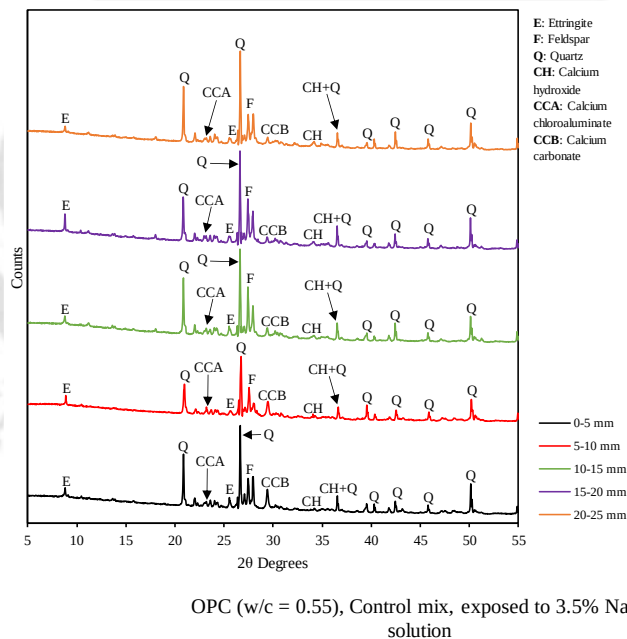


Fig. 7.46 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, 15-20 mm and 20-25 mm from the exposure surface of control concrete made from OPC at w/c of 0.55, and exposed to 3.5% NaCl solution

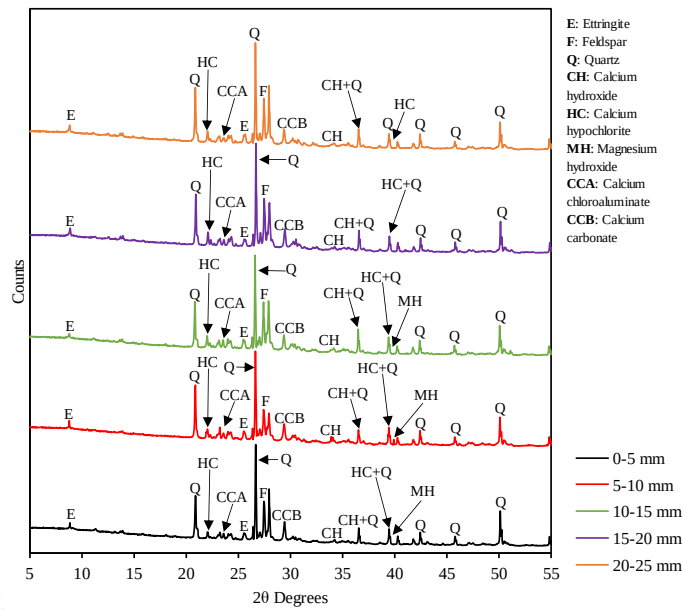


Fig. 7.47 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, 15-20 mm and 20-25 mm from the exposure surface of OPC concrete admixed with 3% NaNO₂ at w/c of 0.55, and exposed to 3.5% MgCl₂ solution

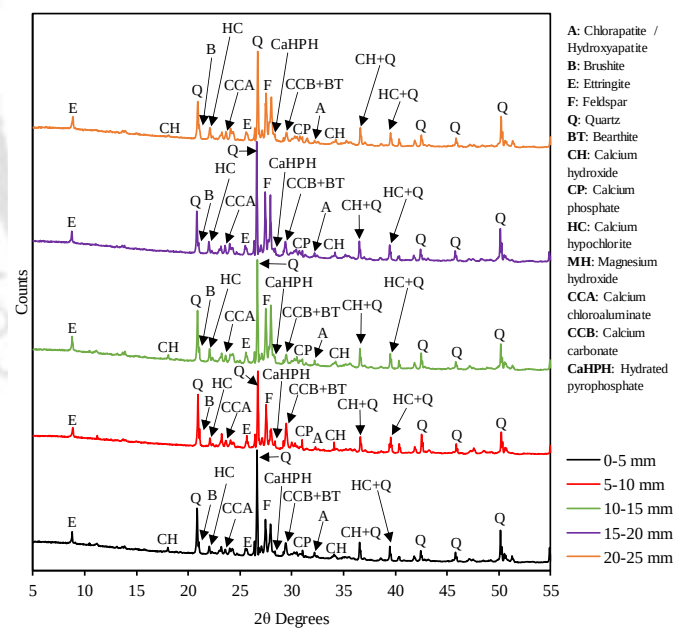


Fig. 7.48 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, 15-20 mm and 20-25 mm from the exposure surface of OPC concrete admixed with 3% DHP at w/c of 0.55, and exposed to 3.5% CaCl₂ solution

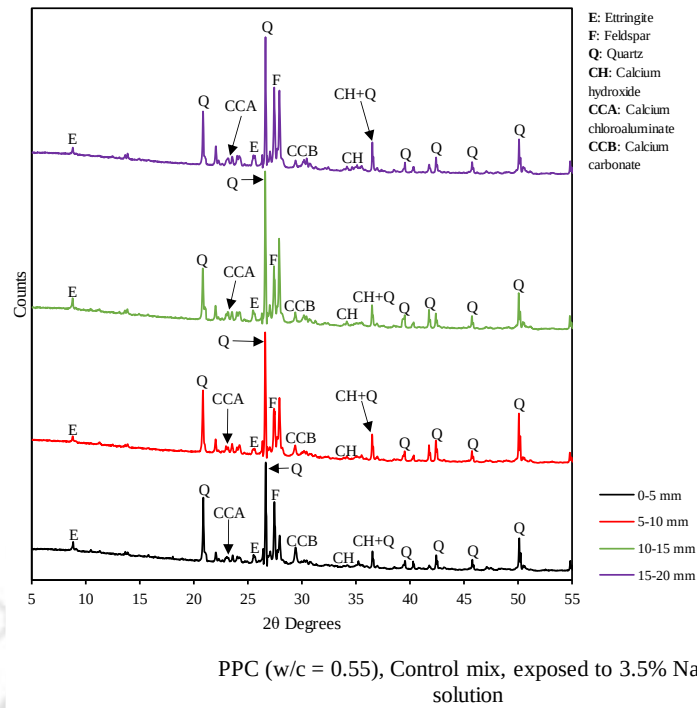


Fig. 7.49 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, and 15-20 mm from the exposure surface of control concrete made from PPC at w/c of 0.55, and exposed to 3.5% NaCl solution

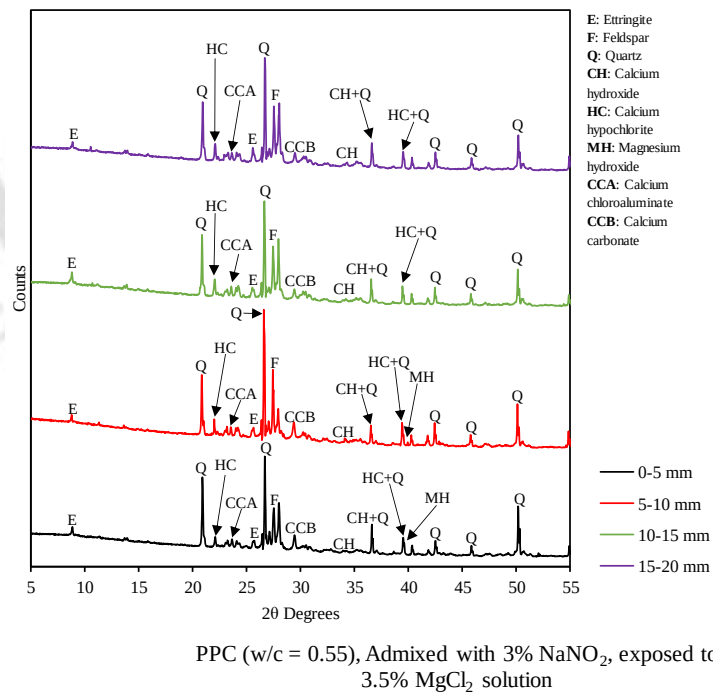


Fig. 7.50 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, and 15-20 mm from the exposure surface of PPC concrete admixed with 3% NaNO_2 at w/c of 0.55, and exposed to 3.5% MgCl_2 solution

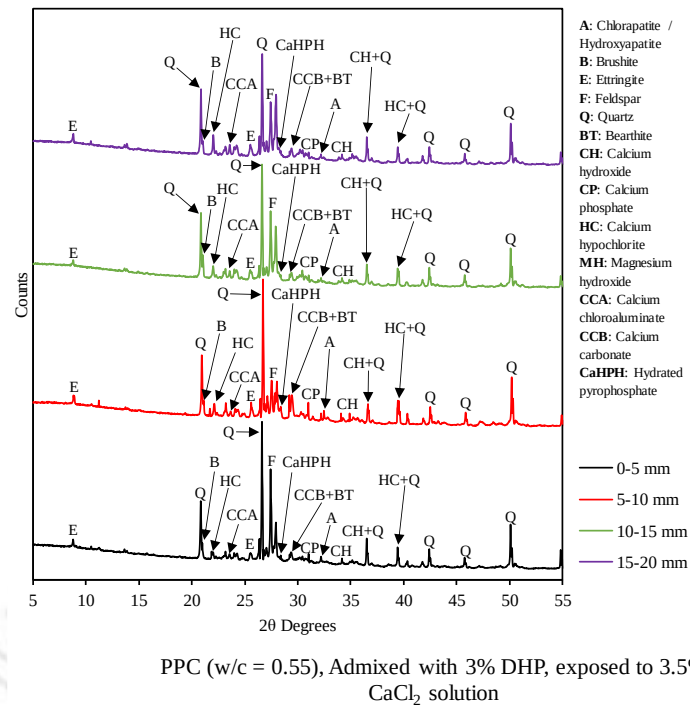


Fig. 7.51 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, and 15-20 mm from the exposure surface of PPC concrete admixed with 3% DHP at w/c of 0.55, and exposed to 3.5% CaCl₂ solution

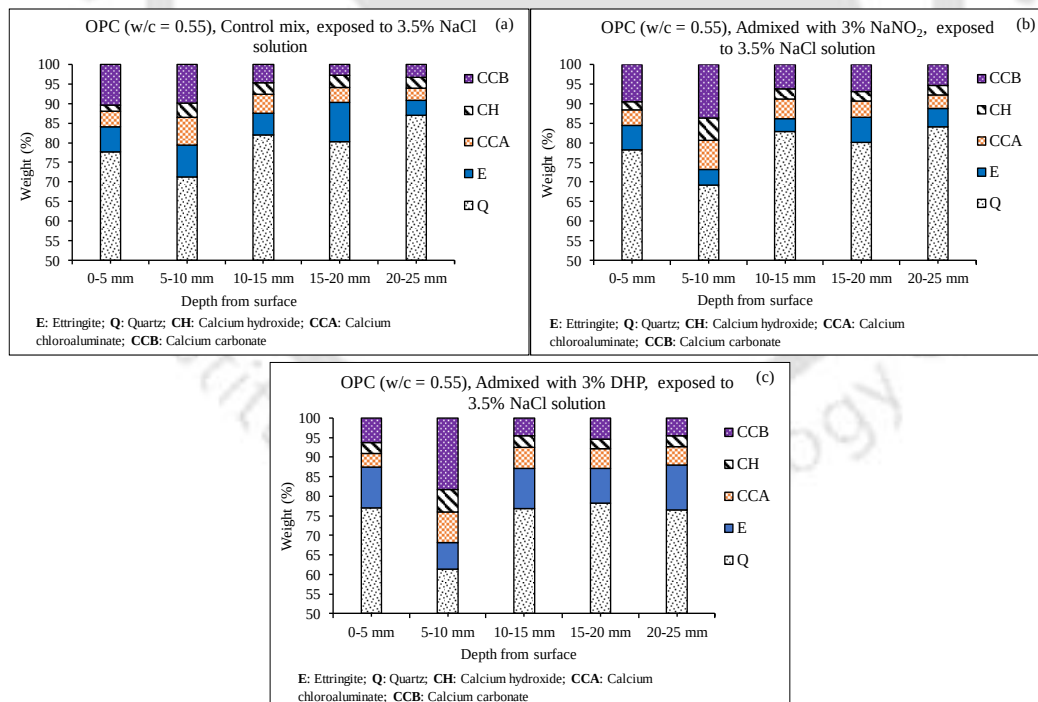


Fig. 7.52 Weight (%) of compounds from XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, 15-20 mm, and 20-25 mm from the exposure surface of OPC concrete at w/c of 0.55, and exposed to 3.5% NaCl solution: (a) control mix, (b) concrete admixed with 3% NaNO₂, and (c) concrete admixed with 3% DHP

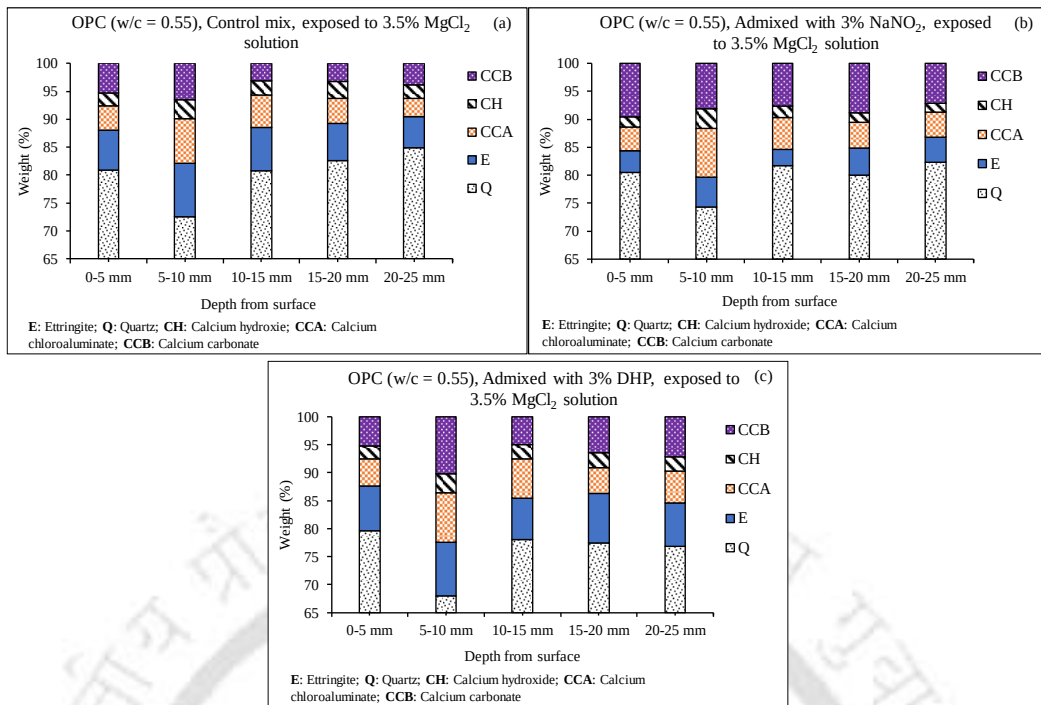


Fig. 7.53 Weight (%) of compounds from XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, 15-20 mm, and 20-25 mm from the exposure surface of OPC concrete at w/c of 0.55, and exposed to 3.5% $MgCl_2$ solution: (a) control mix, (b) concrete admixed with 3% $NaNO_2$, and (c) concrete admixed with 3% DHP

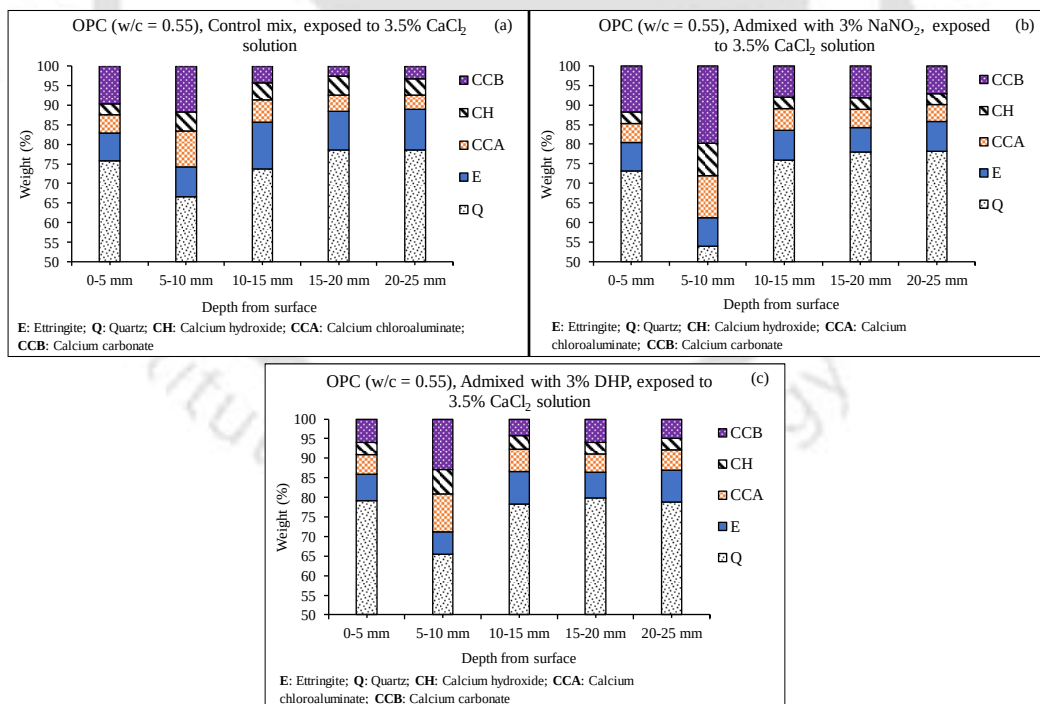


Fig. 7.54 Weight (%) of compounds from XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, 15-20 mm, and 20-25 mm from the exposure surface of OPC concrete at w/c of 0.55, and exposed to 3.5% $CaCl_2$ solution: (a) control mix, (b) concrete admixed with 3% $NaNO_2$, and (c) concrete admixed with 3% DHP

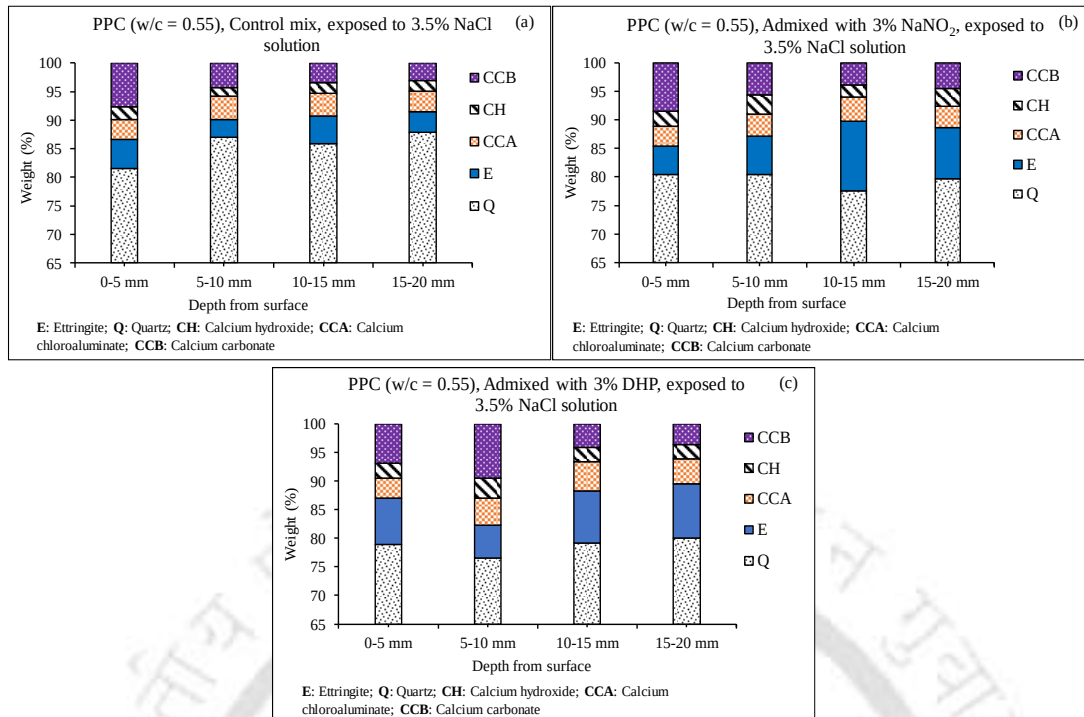


Fig. 7.55 Weight (%) of compounds from XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, and 15-20 mm from the exposure surface of PPC concrete at w/c of 0.55, and exposed to 3.5% NaCl solution: (a) control mix, (b) concrete admixed with 3% NaNO₂, and (c) concrete admixed with 3% DHP

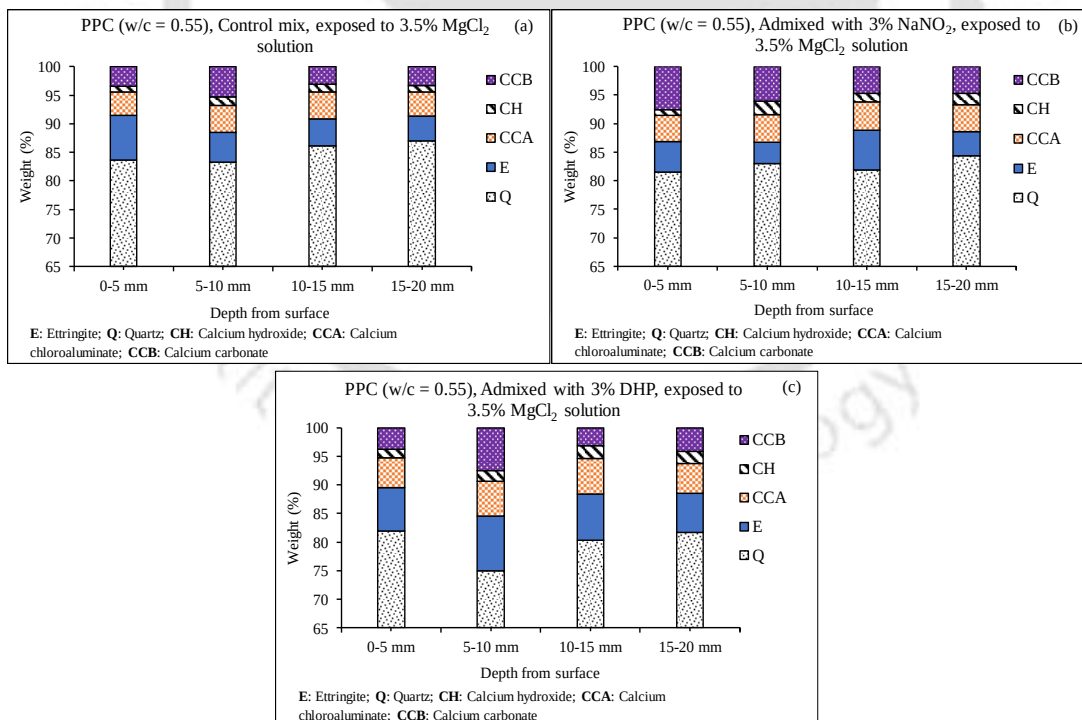


Fig. 7.56 Weight (%) of compounds from XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, and 15-20 mm from the exposure surface of PPC concrete at w/c of 0.55, and exposed to 3.5% MgCl₂ solution: (a) control mix, (b) concrete admixed with 3% NaNO₂, and (c) concrete admixed with 3% DHP

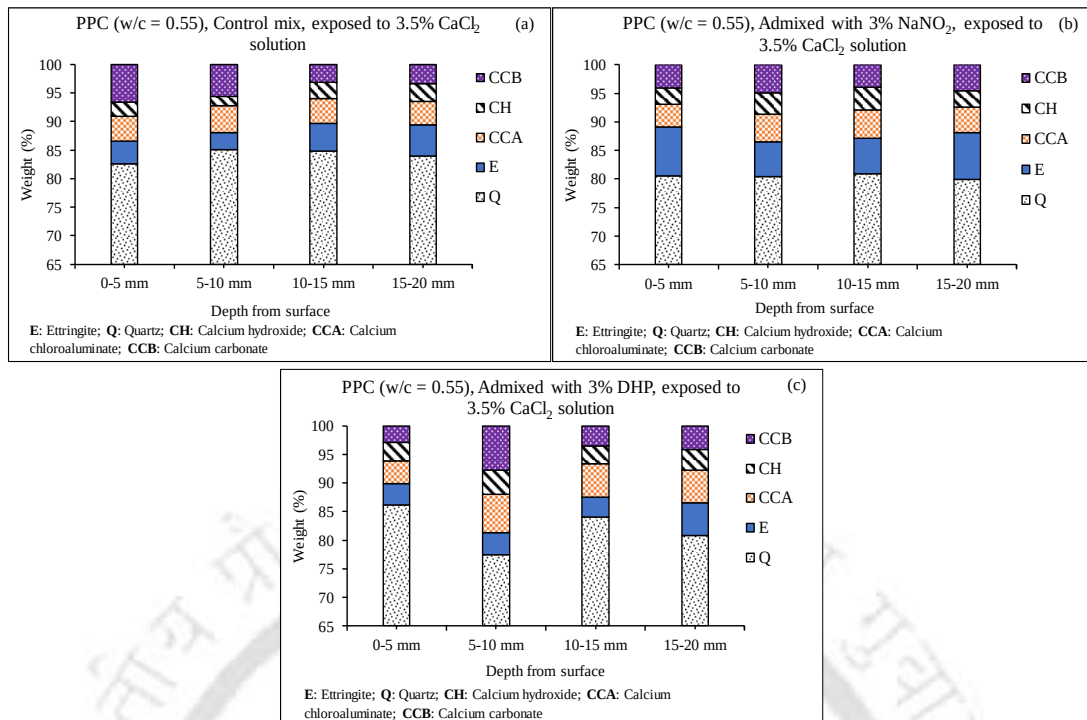


Fig. 7.57 Weight (%) of compounds from XRD patterns at depth intervals of 0-5 mm, 10-15 mm, and 15-20 mm from the exposure surface of PPC concrete at w/c of 0.55, and exposed to 3.5% CaCl_2 solution: (a) control mix, (b) concrete admixed with 3% NaNO_2 , and (c) concrete admixed with 3% DHP

From the weight (%) of the compounds obtained from the XRD analysis (shown in Fig. 7.52 to Fig. 7.57), it is observed that there was no significant difference in the amount of calcium hydroxide (CH) with increase in depth from the exposure surface of concrete exposed to chloride solutions except at the depth interval of 5-10 mm, regardless of cement type, presence of corrosion inhibitors and chloride salt in the exposure solution. This may be attributed to the effect of less variation in the consumption of calcium hydroxide among different depth intervals in the formation of different compounds in control concrete and that admixed with corrosion inhibitors in case of exposure to chloride solutions. However, at depth interval of 5-10 mm, the weight (%) of calcium hydroxide was comparatively higher as compared to all other depth intervals. The higher calcium hydroxide content at depth interval of 5-10 mm from the exposure surface may be ascribed to its buildup in this depth interval as a result of leaching of calcium hydroxide in the presence of chloride ions from interior part (i.e., beyond depth of 10 mm from the exposure surface) toward the surface region of concrete.

From Fig. 7.52 to Fig. 7.57, it is observed that the weight (%) calcium chloroaluminate (obtained from XRD analysis) in concrete increased up to the depth interval of 5-10 mm

from the exposure surface followed by a decrease thereafter with increase in depth irrespective of cement type, presence of corrosion inhibitors, and cation type of chloride salt in chloride exposure solutions. As discussed earlier in Section 7.3.1, the free chloride ion content of concrete decreased with increase in depth interval from the exposure surface i.e., the free chloride ion content was higher in the depth interval of 0-5 mm from the exposure surface, and decreased thereafter with increase in depth. Further, in some of the specimens (as discussed earlier in Section 7.3.1), convection zone was observed in the depth interval of 0-5 mm where the free chloride content was lower as compared to that in the adjacent depth interval i.e., 5-10 mm from the exposure surface. Thus, lower CCA content in the depth interval of 0-5 mm from the exposure surface may be attributed to the effect of lower extent of reaction of chloride ions with C_3A , and also due to the effect of presence of convection zone. The higher amount of calcium chloroaluminate (CCA) in the depth interval of 5-10 mm from the exposure surface may be due to the effect of reaction of chloride ions with C_3A to a comparatively higher extent. Further, lower calcium chloroaluminate content at higher depth intervals i.e., beyond 10 mm from the exposure surface may be ascribed to the penetration of lower amount of chloride ions to higher depth intervals from the exposure surface of concrete thereby resulting in lower extent of reaction of chloride ions with C_3A . From Fig. 7.52 to Fig. 7.57, it is observed that there was no systematic variation in weight (%) of ettringite with increase in depth from the surface of concrete for both cements, corrosion inhibitors, and all chloride exposure solutions. This is attributed to effect of variations in the extent of reaction of gypsum with C_3A as well as that in the extent of solubility of ettringite in the presence of chloride ions among different depth intervals in concrete.

7.5.2 Fourier transform infrared (FTIR) spectroscopy

To determine the functional groups associated with different compounds present in concrete, FTIR spectroscopy was performed on concrete made from OPC, and PPC at w/c of 0.55; admixed with, and without corrosion inhibitors and exposed to chloride, and composite chloride-sulfate solutions. The obtained FTIR spectra are presented in Fig. 7.58, and Fig. 7.60 for OPC, and in Fig. 7.59, and Fig. 7.61 for PPC concrete mixes. The FTIR spectra shown in Fig. 7.58 to Fig. 7.61 correspond to the concrete powder samples obtained from the depth interval of 5-10 mm from the exposure surface of concrete.

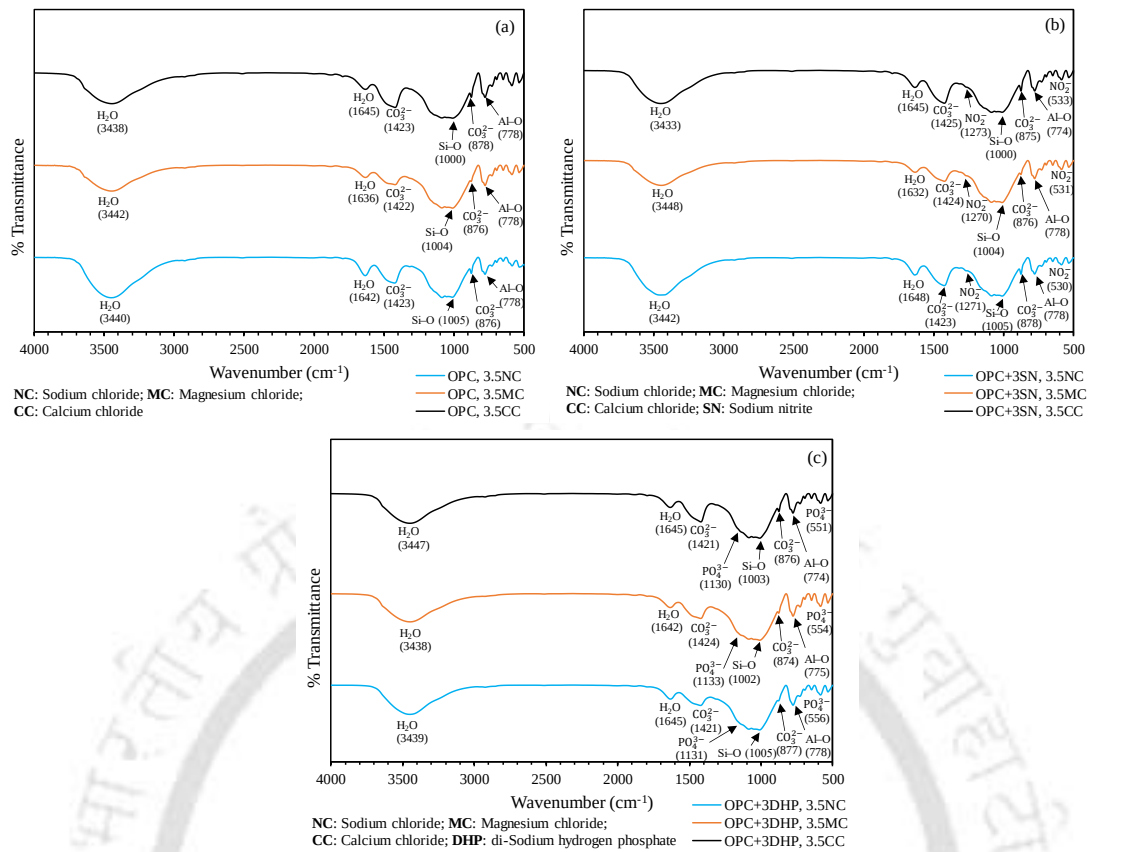
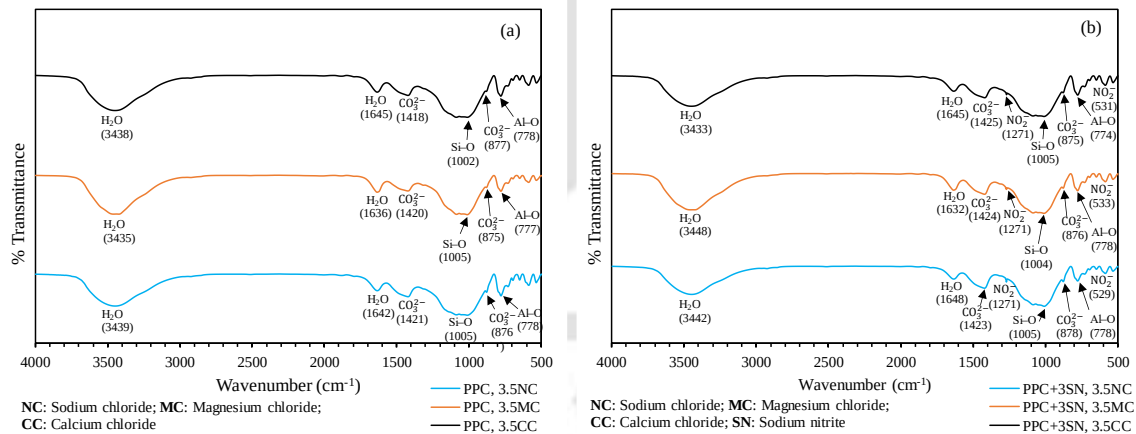


Fig. 7.58 FTIR spectra of OPC concrete at w/c of 0.55, and exposed to 3.5% chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂): (a) control mix, (b) concrete admixed with 3% NaNO₂, and (c) concrete admixed with 3% DHP



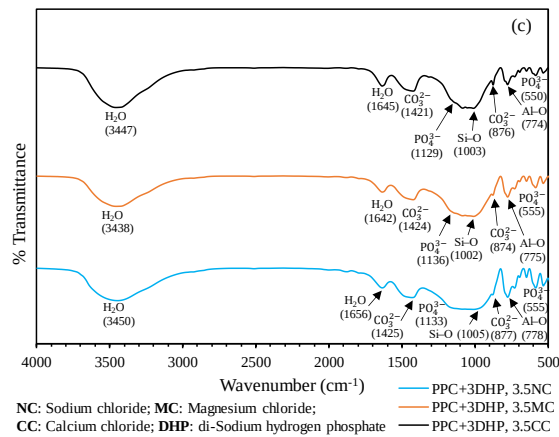


Fig. 7.59 FTIR spectra of PPC concrete at w/c of 0.55, and exposed to 3.5% chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂): (a) control mix, (b) concrete admixed with 3% NaNO₂, and (c) concrete admixed with 3% DHP

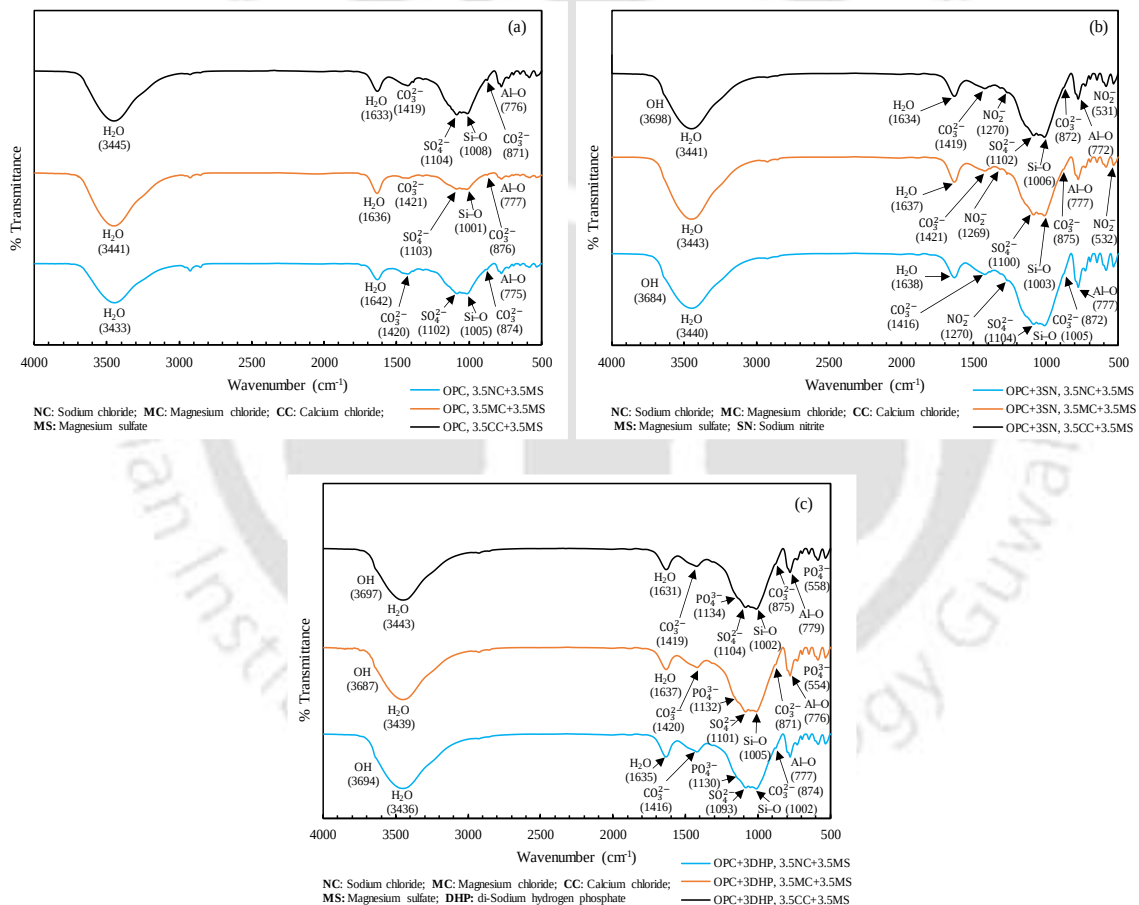


Fig. 7.60 FTIR spectra of OPC concrete at w/c of 0.55, and exposed to composite chloride-sulfate solutions: (a) control mix, (b) concrete admixed with 3% NaNO₂, and (c) concrete admixed with 3% DHP

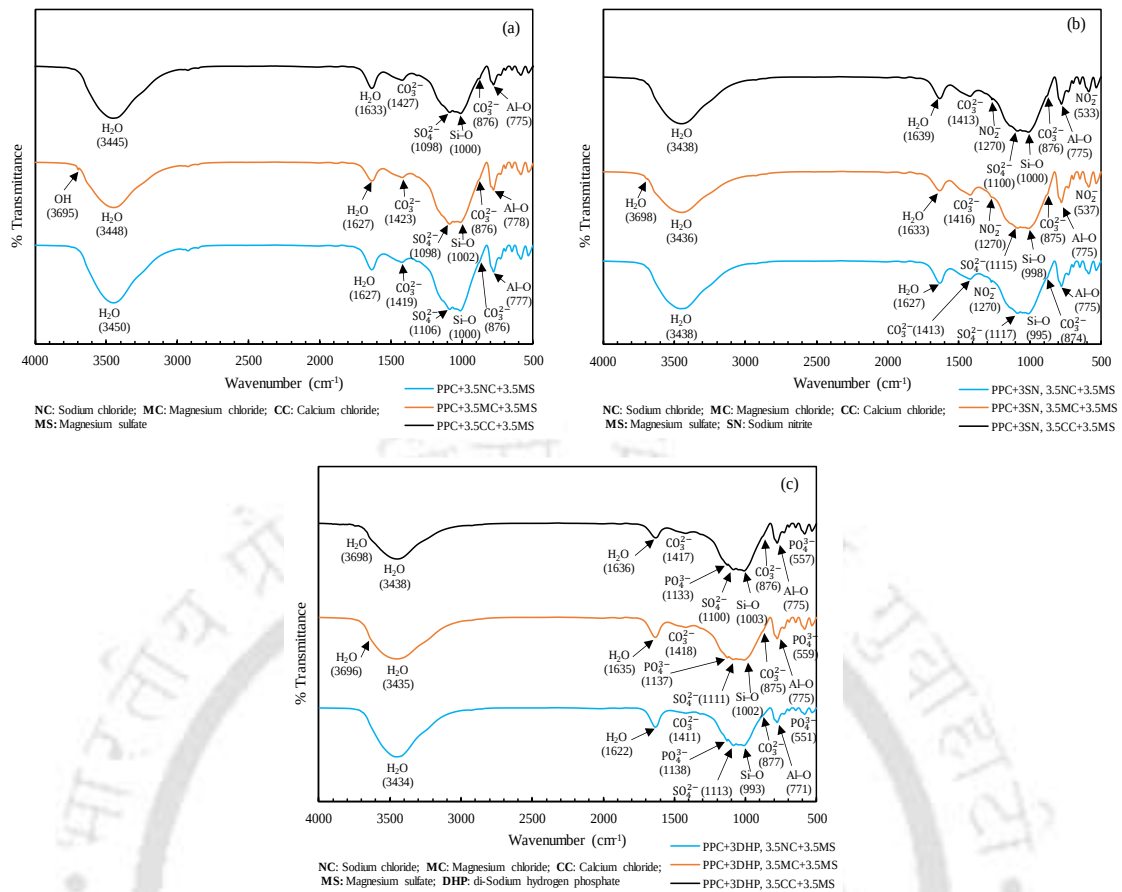


Fig. 7.61 FTIR spectra of PPC concrete at w/c of 0.55, and exposed to composite chloride-sulfate solutions: (a) control mix, (b) concrete admixed with 3% NaNO₂, and (c) concrete admixed with 3% DHP

In Fig. 7.58 to Fig. 7.61, the wide bands observed between 3433 - 3448 cm⁻¹ in OPC concrete, and those between 3433 - 3450 cm⁻¹ in PPC concrete can be attributed to the stretching vibrations of O-H band associated with structural water present in cement hydration products. The bands observed from 1631 - 1648 cm⁻¹ in OPC concrete, and that from 1622 - 1656 cm⁻¹ in PPC concrete correspond to the bending vibration of O-H band related to interlayer water present in the cement hydration products [105, 171, 174, 175]. In OPC concrete, the strong bands between 1421 - 1425 cm⁻¹, and that between 1411 - 1427 cm⁻¹ in PPC concrete are ascribed to ν_3 vibration of CO₃²⁻, which confirms the presence of CaCO₃ in concrete mixes [105, 171, 174, 175, 177]. In addition, the out-of-plane bending (ν_2) related to CO₃²⁻ appears in the range of 871 - 878 cm⁻¹ in both OPC and PPC concrete mixes [105, 173-175]. The presence of ettringite in the concrete is confirmed by the Al-O peaks observed between 771 - 778 cm⁻¹ in both OPC and PPC concrete mixes exposed to chloride, and composite chloride-sulfate solutions [172]. The bands ranging from 993 - 1008 cm⁻¹ in OPC and PPC concrete mixes can be ascribed to asymmetric stretching

vibration of Si-O that correspond to calcium silicate hydrate (C-S-H) [174, 175]. In case of exposure to composite chloride-sulfate solutions, the strength of Si-O band in the concrete exposed to $\text{MgCl}_2 + \text{MgSO}_4$ solution was slightly lower than those exposed to $\text{NaCl} + \text{MgSO}_4$ and $\text{CaCl}_2 + \text{MgSO}_4$ solutions. This may be attributed to comparatively higher decomposition of C-S-H due to MgSO_4 attack in the concrete exposed to $\text{MgCl}_2 + \text{MgSO}_4$ solution as compared to $\text{NaCl} + \text{MgSO}_4$ and $\text{CaCl}_2 + \text{MgSO}_4$ solutions [47]. The use of sodium nitrite in concrete is responsible for the asymmetric stretching vibration, and bending vibration of nitrite observed in the range of $1269 - 1273 \text{ cm}^{-1}$, and $530 - 537 \text{ cm}^{-1}$ respectively in the FTIR spectra shown in Fig. 7.58 (b), Fig. 7.59 (b), Fig. 7.60 (b), and Fig. 7.61 (b) [105]. In addition, the peaks appeared in the range of $1129 - 1139 \text{ cm}^{-1}$, and $550 - 559 \text{ cm}^{-1}$ in the FTIR spectra shown in Fig. 7.58 (c), Fig. 7.59 (c), Fig. 7.60 (c), and Fig. 7.61 (c) correspond to the presence of phosphates in the concrete admixed with DHP [105].

In most of the concrete mixes exposed to composite chloride-sulfate solutions, the peaks observed in the range of $3684 - 3698 \text{ cm}^{-1}$ (Fig. 7.60 and Fig. 7.61) are associated with the stretching vibration of O-H band in brucite (magnesium hydroxide) [62]. Further, in case of exposure to composite chloride-sulfate solutions (Fig. 7.60 and Fig. 7.61), the peaks appeared in the range of $1093 - 1113 \text{ cm}^{-1}$ correspond to the asymmetric stretching vibration of SO_4^{2-} group, which confirms the presence of gypsum and ettringite phases in concrete [47, 62].

7.5.3 Field emission scanning electron microscope (FESEM) analysis

The obtained typical FESEM images of concrete prepared from OPC, and PPC at w/c of 0.55; admixed with, and without corrosion inhibitors; and exposed to chloride, and composite chloride-sulfate solutions are shown in Fig. 7.62 to Fig. 7.65. The FESEM images shown in Fig. 7.62 to Fig. 7.65 correspond to the concrete powder samples obtained from the depth interval of 5-10 mm from the exposure surface of concrete.

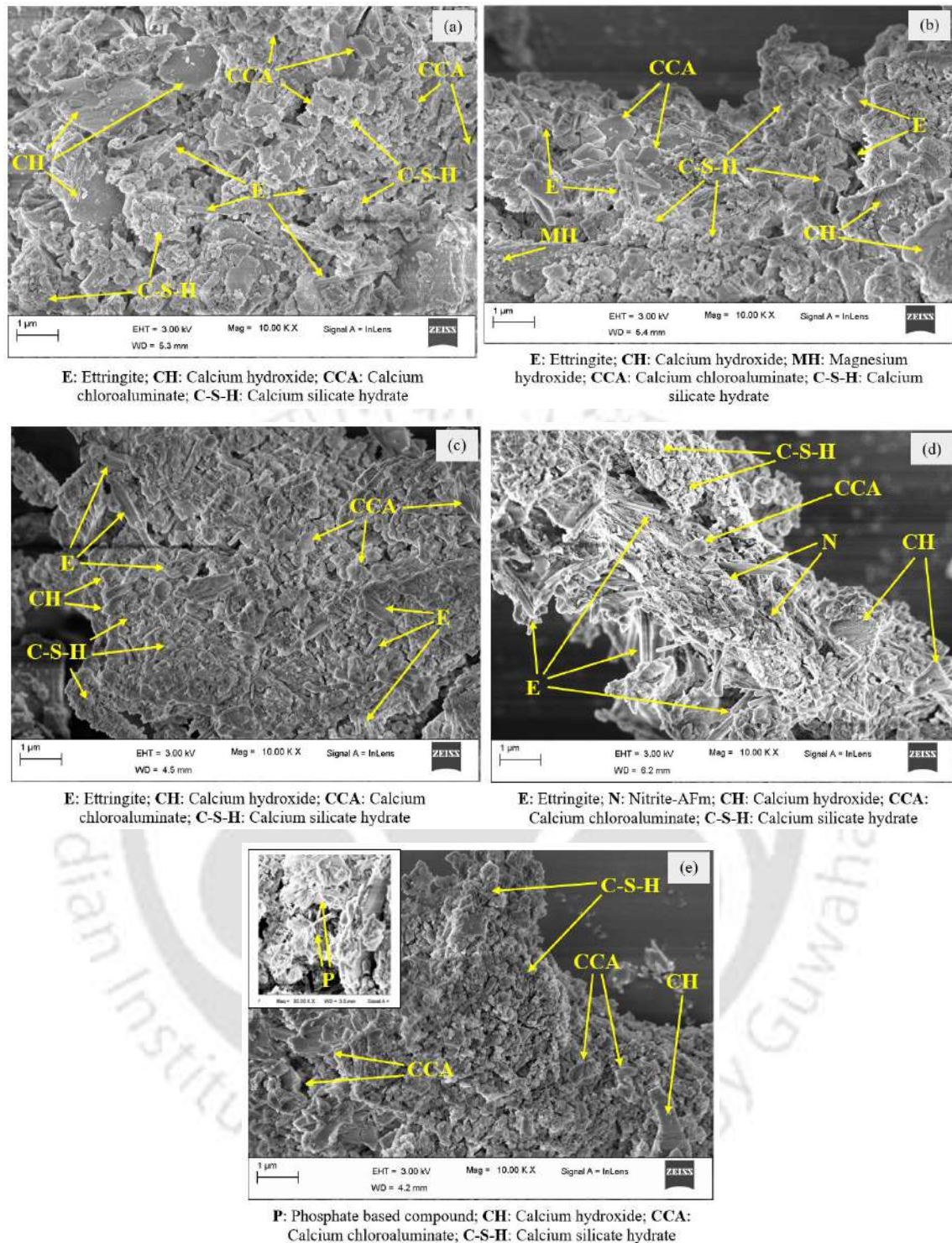


Fig. 7.62 FESEM images of OPC concrete at w/c of 0.55: (a) control mix exposed to 3.5% NaCl solution, (b) control mix exposed to 3.5% MgCl_2 solution, (c) control mix exposed to 3.5% CaCl_2 solution, (d) concrete with 3% NaNO_2 , exposed to 3.5% NaCl solution, and (e) concrete with 3% DHP, exposed to 3.5% NaCl solution

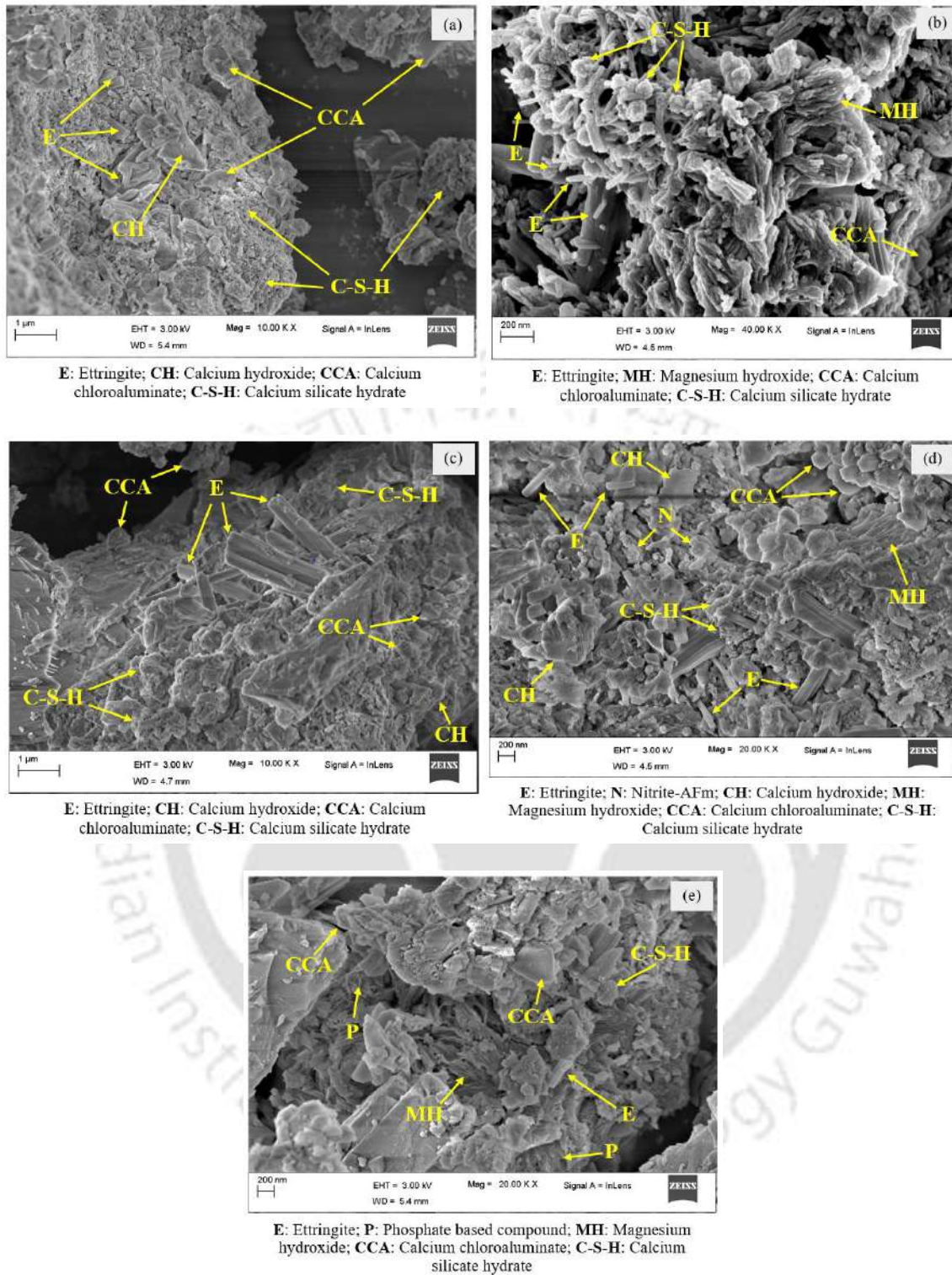


Fig. 7.63 FESEM images of PPC concrete at w/c of 0.55: (a) control mix exposed to 3.5% NaCl solution, (b) control mix exposed to 3.5% MgCl₂ solution, (c) control mix exposed to 3.5% CaCl₂ solution, (d) concrete with 3% NaNO₂, exposed to 3.5% MgCl₂ solution, and (e) concrete with 3% DHP, exposed to 3.5% MgCl₂ solution

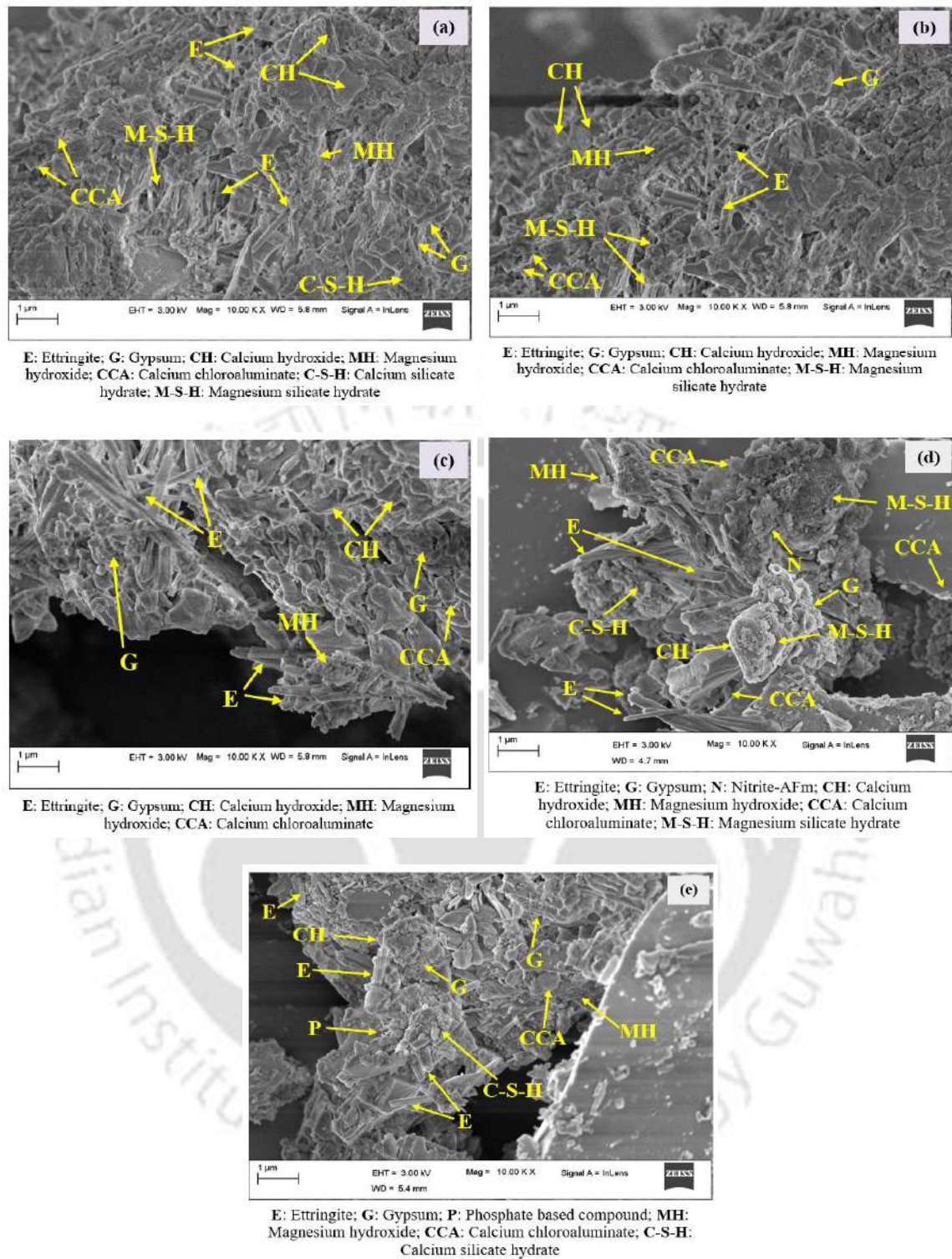


Fig. 7.64 FESEM images of OPC concrete at w/c of 0.55: (a) control mix exposed to 3.5% NaCl+3.5% MgSO₄ solution, (b) control mix exposed to 3.5% MgCl₂+3.5% MgSO₄ solution, (c) control mix exposed to 3.5% CaCl₂+3.5% MgSO₄ solution, (d) concrete with 3% NaNO₂, exposed to 3.5% CaCl₂+3.5% MgSO₄ solution, and (e) concrete with 3% DHP, exposed to 3.5% CaCl₂+3.5% MgSO₄ solution

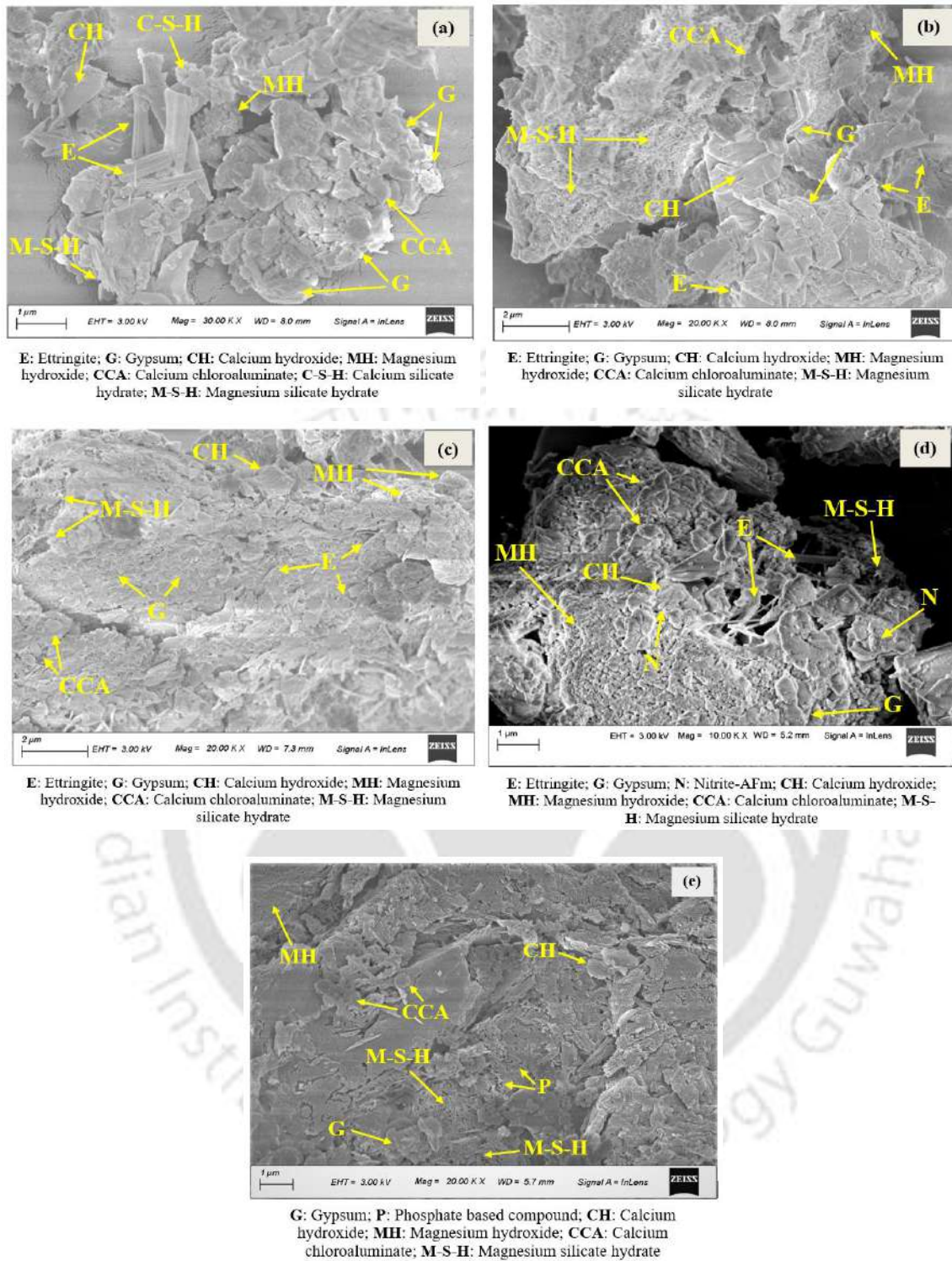


Fig. 7.65 FESEM images of PPC concrete at w/c of 0.55: (a) control mix exposed to 3.5% NaCl+3.5% MgSO₄ solution, (b) control mix exposed to 3.5% MgCl₂+3.5% MgSO₄ solution, (c) control mix exposed to 3.5% CaCl₂+3.5% MgSO₄ solution, (d) concrete with 3% NaNO₂, exposed to 3.5% NaCl+3.5% MgSO₄ solution, and (d) concrete with 3% DHP, exposed to 3.5% NaCl+3.5% MgSO₄ solution

From the FESEM images shown in Fig. 7.62 to Fig. 7.65, the formation of calcium silicate hydrate (C-S-H), ettringite (E), calcium hydroxide (CH), and calcium chloroaluminate (CCA) in the concrete mixes are confirmed, which further substantiates the results obtained from the XRD analysis. In the FESEM images, the cotton-shaped structures were identified as C-S-H [193], whereas the needle shaped crystal structures were identified as ettringite in both OPC and PPC concrete [204] irrespective of presence of corrosion inhibitors, and type of chloride salt in both chloride, and composite chloride-sulfate solutions. The formation of additional C-S-H gel as a result of pozzolanic reaction leads to denser microstructure in PPC concrete as compared to OPC concrete as evident from the FESEM images shown in Fig. 7.62 to Fig. 7.65. The large size hexagonal shape crystals were identified as calcium hydroxide (CH) in OPC and PPC concrete as observed from Fig. 7.62 to Fig. 7.65. Further, lesser calcium hydroxide crystals were observed in PPC concrete as compared to OPC concrete (Fig. 7.62 to Fig. 7.65), which may be due to the consumption of calcium hydroxide in the pozzolanic reaction in PPC concrete. The formation of calcium chloroaluminate (CCA) in concrete is confirmed by small hexagonal slice crystals in the FESEM images shown in Fig. 7.62 to Fig. 7.65. The formation of calcium chloroaluminate is more in OPC concrete as compared to PPC concrete as noted from the FESEM images shown in Fig. 7.62 to Fig. 7.65. The rosette-like clusters of magnesium hydroxide (brucite) crystals were observed in the FESEM images of concrete mixes exposed to MgCl_2 solution, and those exposed to composite chloride-sulfate solutions (Fig. 7.62 (b), Fig. 7.63 (b, d, e), Fig. 7.64, and Fig. 7.65). In addition, in the concrete exposed to composite chloride-sulfate solutions, fibrous magnesium silicate hydrate (M-S-H) gel formation, and layers of ice like plate of gypsum crystals due to magnesium sulfate attack were observed in the FESEM images shown in Fig. 7.64 and, Fig. 7.65. Besides, the formation of M-S-H gel was comparatively more in the concrete exposed to $\text{MgCl}_2 + \text{MgSO}_4$ solution as compared to $\text{NaCl} + \text{MgSO}_4$ and $\text{CaCl}_2 + \text{MgSO}_4$ solutions as observed from Fig. 7.64, and Fig. 7.65. The reason behind more formation of M-S-H in the concrete exposed to $\text{MgCl}_2 + \text{MgSO}_4$ solution may be due to the presence of higher amount of magnesium hydroxide in the concrete. As already discussed in XRD analysis (Section 7.5.1.1), the formation of magnesium hydroxide was higher in the concrete exposed to $\text{MgCl}_2 + \text{MgSO}_4$ solution as compared to $\text{NaCl} + \text{MgSO}_4$ and $\text{CaCl}_2 + \text{MgSO}_4$ solutions.

In Fig. 7.62 (d), Fig. 7.63 (d), Fig. 7.64 (d), and Fig. 7.65 (d), large number of petal shaped crystals was observed in the concrete containing NaNO_2 , which may be a form of nitrite-

AFm [132]. Further, in the concrete containing DHP, rod-shaped structures were observed in the FESEM images (Fig. 7.62 (e), Fig. 7.63 (e), Fig. 7.64 (e), and Fig. 7.65 (e)), which cover and block the pores in concrete thereby minimizing the ingress of chloride ions [25]. These rod-shaped structures are related to the phosphate based compounds formed in concrete containing DHP [25].

7.6 Summary

The results of chloride analysis indicated that in control concrete as well as that containing corrosion inhibitors, the free chloride ion content and apparent chloride diffusion coefficient (D_{app}) were higher in case of exposure to NaCl solution than $CaCl_2$ and $MgCl_2$ solutions for both cements and w/c. In case of composite chloride-sulfate solutions, the free chloride content was higher in the concrete exposed to $CaCl_2+MgSO_4$ solution as compared to $NaCl+MgSO_4$ and $MgCl_2+MgSO_4$ solutions, whereas the apparent chloride diffusion coefficient was higher in case of exposure to $MgCl_2+MgSO_4$ solution than other composite chloride-sulfate solutions for control concrete as well as that containing corrosion inhibitors for both cements and w/c. The free chloride ion content and apparent chloride diffusion coefficient were lower in the concrete admixed with corrosion inhibitors as compared to control concrete for chloride as well as composite chloride-sulfate solutions. The apparent chloride diffusion coefficient (D_{app}) was mostly higher in the concrete containing DHP as compared to that containing $NaNO_2$ for exposure to chloride and composite chloride-sulfate solutions. The free chloride ion content was higher in PPC concrete as compared to OPC concrete at lower depth intervals from the exposure surface, whereas the opposite variation in free chloride content was observed between OPC and PPC at higher depth intervals in all concrete mixes exposed to chloride and composite chloride-sulfate solutions. Between OPC and PPC, the D_{app} was higher in OPC concrete as compared to PPC concrete regardless of w/c, presence of corrosion inhibitors, and cation type of chloride salt in chloride and composite chloride-sulfate solutions.

For chloride solutions, the chloride binding capacity of concrete was higher in case of exposure to $CaCl_2$ solution than other chloride solutions, whereas in case of exposure to composite chloride-sulfate solutions, the chloride binding capacity was higher when exposed to $NaCl+MgSO_4$ solution as compared to other composite chloride-sulfate solutions for control concrete as well as that admixed with corrosion inhibitors. Further, the chloride binding capacity was higher in OPC concrete as compared to PPC concrete regardless of w/c, presence of corrosion inhibitors, and cation type of chloride salt in both

chloride and composite chloride-sulfate solutions. Between corrosion inhibitors, concrete containing DHP exhibited higher chloride binding capacity as compared to NaNO_2 in case of exposure to chloride solutions, whereas in case of exposure to composite chloride-sulfate solutions, the opposite variation in chloride binding capacity was observed between DHP and NaNO_2 .

The results of XRD, FTIR, and FESEM analyses indicated the formation of various compounds in control concrete and that admixed with corrosion inhibitors for exposure to chloride and composite chloride-sulfate solutions. The variations in chloride binding capacity of concrete with cement type, cation type of chloride salt in chloride and composite chloride-sulfate exposure solutions, and corrosion inhibitors are in line with the variations in the formations of calcium chloroaluminate as observed from the XRD analysis. The results of XRD analysis indicated higher calcium hydroxide content in the concrete exposed to chloride solutions as compared to composite chloride-sulfate solutions. The results of XRD, FTIR, and FESEM analyses indicated the formation of magnesium hydroxide in the concrete exposed to MgCl_2 and $\text{MgCl}_2+\text{MgSO}_4$ solutions. Further, the formation of magnesium hydroxide was higher in the concrete exposed to $\text{MgCl}_2+\text{MgSO}_4$ solution as compared to other composite chloride-sulfate solutions as observed from the results of XRD analysis. The FESEM images indicated more formation of C-S-H gel in PPC concrete as compared to OPC concrete.



Conclusions and Suggestions for Further Study

8.1 General

In this chapter, the conclusions obtained from the present research work are presented. Based on the results obtained from the experimental investigation followed by discussion, conclusions have been drawn on the variations in compressive strength of concrete, and corrosion behaviour of steel reinforcement in concrete powder electrolyte solution (CPES) admixed with different chloride salts and corrosion inhibitors. Further, on the basis of the results obtained from corrosion tests carried out on steel reinforcement embedded in cylindrical reinforced concrete specimens exposed to internal chloride, and external chloride and composite chloride-sulfate environment, conclusions on the effects of cement type, w/c, corrosion inhibitors, and cation type of chloride salts on corrosion behaviour of steel reinforcement have been drawn. Besides, the conclusions on variations in free chloride profile, apparent chloride diffusion coefficient, and chloride binding capacity of concrete exposed to chloride and composite chloride-sulfate solutions have been obtained. In addition, the conclusions on the effects of mix parameters (i.e., cement type and w/c), corrosion inhibitors, exposure solution, and cation type of chloride salts on the variations in microstructure of concrete have also been obtained.

8.2 Conclusions from compressive strength of concrete

- The addition of chloride salts increased the compressive strength, whereas the addition of corrosion inhibitors decreased the compressive strength of concrete than control mix for both cements.
- The concrete admixed with di-Sodium hydrogen phosphate (DHP) showed lower compressive strength than that admixed with sodium nitrite (NaNO_2) for both types of cement irrespective of presence and type of chloride salts.
- The compressive strength of concrete for both OPC and PPC was greatly affected by the cation type associated with chloride salts with the trend of compressive strength: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$ irrespective of cement type and corrosion inhibitors.

8.3 Conclusions from corrosion behaviour of steel reinforcement in concrete powder electrolyte solution (CPES) in the presence of corrosion inhibitors

- The passivity range of reinforcing steel in the concrete powder electrolyte solution (CPES) admixed with CaCl_2 was higher in comparison to MgCl_2 and NaCl irrespective of cement type. However, in the presence of corrosion inhibitors, the passivity range of steel reinforcement was higher in case of NaCl than CaCl_2 and MgCl_2 . Thus, the effect of cation type associated with chloride ions on passivity of steel reinforcement was influenced by the presence of corrosion inhibitors.
- The presence of corrosion inhibitors increased the passivity of steel in the CPES admixed with chloride salts. In the presence of chloride salts (i.e., NaCl , MgCl_2 , and CaCl_2), NaNO_2 was more effective in enhancing the passivity of steel than DHP.
- The passivity range of reinforcing steel in the CPES prepared from OPC was higher in comparison to that prepared from PPC irrespective of chloride salts and corrosion inhibitors.
- The cation type associated with chloride salts influenced the free chloride ion (C_F) and bound chloride ion (C_B) contents of concrete. The trends of free chloride ion (C_F) and bound chloride ion (C_B) contents were C_F : $\text{NaCl} > \text{CaCl}_2 > \text{MgCl}_2$; and C_B : $\text{CaCl}_2 > \text{MgCl}_2 > \text{NaCl}$ for both types of cement and corrosion inhibitors.
- The formation of various compounds in the concrete as indicated by the XRD patterns were further corroborated with the FTIR spectra showing the functional groups associated with these compounds formed in concrete.
- The results of XRD analysis indicated the formation of higher amount of calcium chloroaluminate in the concrete admixed with CaCl_2 as compared to MgCl_2 and NaCl irrespective of cement type, and presence and type of corrosion inhibitors. Further, the XRD analysis showed the formation of hydrated pyrophosphate and brushite in the concrete admixed with DHP, which is responsible for reduction in compressive strength of concrete containing DHP than control concrete.
- In the concrete admixed with MgCl_2 and CaCl_2 , the formation of calcium hypochlorite was confirmed from the obtained results of XRD analysis for both cements and corrosion inhibitors. The amount of calcium hypochlorite was higher in the concrete admixed with MgCl_2 than that admixed with CaCl_2 .

8.4 Conclusions from corrosion behaviour of steel reinforcement against internal chloride in concrete containing corrosion inhibitors

- The electrochemical results showed lower probability of occurrence of steel reinforcement corrosion and low corrosion rate in the concrete admixed with chloride salts irrespective of cement type, cation type of chloride salts, and presence and type of corrosion inhibitors.
- Even though, the chloride ions were present in the concrete from the beginning as chloride salts were admixed during the preparation of concrete mixes, the lower extent of corrosion activity of steel reinforcement may be attributed to the significant effect of unavailability of adequate amount of moisture and variations in oxygen level near steel reinforcement in concrete.
- In the concrete mixes admixed with NaCl, the half-cell potential was more negative and corrosion current density was higher at all ages as compared to that admixed with CaCl₂ and MgCl₂ for both OPC and PPC irrespective of corrosion inhibitors.
- Between MgCl₂ and CaCl₂, initially, i.e. up to 224 days from the day of preparation of concrete, MgCl₂ showed more negative half-cell potential and higher corrosion current density as compared to CaCl₂, whereas during later age (i.e., after 224 days), the opposite variation in corrosion parameters was observed between MgCl₂ and CaCl₂ for both cements and corrosion inhibitors.
- Sodium nitrite was more effective in reducing the probability of occurrence of steel bar corrosion and corrosion rate than DHP in the concrete admixed with chloride salts. In most of the cases, concrete admixed chloride salt plus DHP showed more negative half-cell potential and higher corrosion current density as compared to that admixed with only chloride salt.
- In case of exposure to internal chloride, OPC exhibited better performance against corrosion of steel reinforcement as compared to PPC regardless of chloride salts and corrosion inhibitors.
- The addition of NaCl in concrete increased the free chloride ion content and reduced the bound chloride ion content as compared to CaCl₂ and MgCl₂ regardless of cement type and corrosion inhibitors.
- The XRD analysis indicated the formation of higher amount of calcium hypochlorite in MgCl₂ admixed concrete than that admixed with CaCl₂. However, the formation of calcium chloroaluminate was more in CaCl₂ admixed concrete than MgCl₂ admixed concrete.

➤ In chloride contaminated concrete, the addition of NaNO_2 and DHP increased the binding of chloride ions thereby reducing free chloride content near rebar level irrespective of cement type and type of admixed chloride salts. The higher chloride binding in concrete in the presence of corrosion inhibitors was further confirmed from the obtained results of XRD and FESEM analyses, which showed more formation of calcium chloroaluminate in the concrete admixed with corrosion inhibitor plus chloride salt than that admixed with only chloride salt.

8.5 Conclusions from effect of corrosion inhibitors on reinforcing steel corrosion in concrete exposed to external chloride and composite chloride-sulfate solutions

➤ The obtained half-cell potential (E_0) and corrosion current density (I_{corr}) indicated that NaCl is more aggressive in depassivating the reinforcing steel early thereby resulting in reduced corrosion initiation period, and increased corrosion rate as compared to CaCl_2 followed by MgCl_2 for control concrete as well as that admixed with corrosion inhibitors when exposed to chloride solutions.

➤ In case of exposure to composite chloride-sulfate solutions, the corrosion activity of steel reinforcement, as indicated by half-cell potential, and corrosion current density, was higher in the concrete exposed to $\text{CaCl}_2 + \text{MgSO}_4$ solution than $\text{NaCl} + \text{MgSO}_4$ solution followed by $\text{MgCl}_2 + \text{MgSO}_4$ solution over the entire exposure period regardless of cement type, and presence and type of corrosion inhibitors.

➤ In OPC concrete, the specimens exposed to chloride solutions showed higher extent of corrosion as compared to those exposed to composite chloride-sulfate solutions. However, in PPC concrete, the variation in corrosion behavior of steel reinforcement between chloride, and composite chloride-sulfate solutions was not systematic.

➤ For both chloride and composite chloride-sulfate exposure solutions, the addition of corrosion inhibitors i.e., sodium nitrite (NaNO_2), and di-Sodium hydrogen phosphate (DHP) enhanced the resistance of concrete against corrosion of steel reinforcement irrespective of cement type, and cation type of chloride salt in chloride and composite chloride-sulfate solutions.

➤ For chloride exposure conditions, concrete admixed NaNO_2 showed more negative half-cell potential and higher corrosion current density than DHP during the early exposure period whereas the opposite variation was observed during the later exposure period where the difference in corrosion current density between NaNO_2 and DHP was significant. This implies that NaNO_2 exhibited improved resistance against chloride induced corrosion of

steel reinforcement as compared to DHP even in the presence of higher amount of chloride ions near steel reinforcement.

- In case of exposure of concrete to composite chloride-sulfate solutions, the variation in corrosion parameters between the corrosion inhibitors was not systematic.
- The efficiency of both the inhibitors against corrosion increased with increase in their dosage as the half-cell potential became less negative and corrosion current density decreased with increase in the inhibitor dosage.
- Both sodium nitrite, and di-Sodium hydrogen phosphate (DHP) were comparatively more effective against corrosion of steel reinforcement in OPC concrete than PPC concrete irrespective of chloride salt in chloride and composite chloride-sulfate solutions. The formation of denser microstructure in PPC concrete was more dominant in minimizing the extent of corrosion over the effect of corrosion inhibitors as the formation of denser microstructure decreased the ingress of chloride ions thereby resulting in significantly lower corrosion current density in PPC concrete than OPC concrete.
- The extent of corrosion of steel reinforcement in concrete increased with increase in w/c, as indicated by the corrosion parameters, over the entire exposure period for both cements, corrosion inhibitors, and all chloride exposure solutions.
- The addition of corrosion inhibitors in concrete decreased the free chloride content near rebar level as compared to control concrete in case of exposure to chloride as well as composite chloride-sulfate solutions irrespective of cement type and chloride salt in the exposure solutions whereas the opposite variation was observed in bound chloride content between control concrete and that admixed with corrosion inhibitors.
- The free chloride content near steel reinforcement was higher in the concrete containing NaNO_2 whereas the bound chloride content was higher in the concrete containing DHP when exposed to chloride solutions. However, there was no systematic variation in free chloride content, and bound chloride content between the corrosion inhibitors in case of exposure to composite chloride-sulfate solutions.
- Between chloride and composite chloride-sulfate solutions, the free chloride, and bound chloride contents near rebar level were higher in the concrete exposed to chloride solutions as compared to composite chloride-sulfate solutions irrespective of chloride salt in the exposure solutions, cement type, and presence of corrosion inhibitors.
- The amount of calcium hydroxide and calcium chloroaluminate (Friedel's salt) in concrete varied not only with the cement type but also with the cation type associated with

chloride ions as well as with the type of corrosion inhibitor and their admixed dosage as observed from XRD analysis.

➤ The XRD analysis showed mostly more formation of calcium hydroxide, calcium chloroaluminate and ettringite in OPC concrete than PPC concrete irrespective of addition of corrosion inhibitors, and chloride salts in chloride as well as composite chloride-sulfate solutions. These observations from the XRD analysis are further substantiated with the FESEM analysis.

➤ In case of exposure to chloride solutions, the formation of calcium hydroxide, and Friedel's salt were higher in the concrete exposed to CaCl_2 solution as compared to MgCl_2 and NaCl solutions as evident from the results of XRD analysis. In case of exposure to composite chloride-sulfate solutions, the formation of calcium hydroxide, and Friedel's salt were higher in the concrete exposed to $\text{CaCl}_2 + \text{MgSO}_4$ solution, and $\text{NaCl} + \text{MgSO}_4$ solution respectively as compared to other composite chloride-sulfate solutions.

➤ The concrete containing DHP mostly showed higher amount of Friedel's salt as compared to that containing NaNO_2 for both chloride and composite chloride-sulfate solutions. However, the formation of Friedel's salt decreased with increase in dosage of DHP whereas the opposite variation was observed in case of NaNO_2 when exposed to chloride solutions.

8.6 Conclusions from effect of corrosion inhibitors on chloride ingress and chloride binding capacity of concrete exposed to chloride and composite chloride-sulfate solutions

➤ From the obtained free chloride content profile, in some cases, the formation of convection zone was observed near the exposure surface i.e., in the depth interval of 0-5 mm from the exposure surface of concrete in case of exposure to NaCl and MgCl_2 solutions. The formation of convection zone was more noticeable in the concrete exposed to NaCl solution as compared to that exposed to MgCl_2 solution.

➤ The type of cement also influenced the formation of convection zone as the convection zone was more noticeable in PPC concrete as compared to OPC concrete. The formation of convection zone increased with increase in w/c. Besides, the formation of convection zone was more in the concrete containing NaNO_2 as compared to DHP.

➤ For both OPC and PPC, the free chloride ion (C_F) content and apparent chloride diffusion coefficient (D_{app}) of control concrete and those containing NaNO_2 , and DHP are

significantly affected by the cation type of chloride salts. In case of exposure to chloride solutions, the free chloride content at all depth intervals from exposure surface of OPC and PPC concrete admixed with and without NaNO_2 , and DHP decreased in the order of C_F : $\text{NaCl} > \text{CaCl}_2 > \text{MgCl}_2$ for both w/c. Similarly, the chloride diffusion coefficient of concrete decreased in the order of D_{app} : $\text{NaCl} > \text{CaCl}_2 > \text{MgCl}_2$.

➤ In case of exposure to composite chloride-sulfate solutions, the free chloride content at all depth intervals from the exposure surface of concrete decreased in the order of C_F : $\text{CaCl}_2 + \text{MgSO}_4 > \text{NaCl} + \text{MgSO}_4 > \text{MgCl}_2 + \text{MgSO}_4$, whereas the apparent chloride diffusion coefficient decreased in the order of D_{app} : $\text{MgCl}_2 + \text{MgSO}_4 > \text{NaCl} + \text{MgSO}_4 > \text{CaCl}_2 + \text{MgSO}_4$ for both cements, w/c, and irrespective of presence of corrosion inhibitors.

➤ Concrete containing NaNO_2 , and DHP showed lower free chloride ion content as well as lower apparent chloride diffusion coefficient (D_{app}) as compared to control concrete for both OPC and PPC irrespective of cation type of chloride salt in chloride and composite chloride-sulfate solutions.

➤ The average ratios of apparent chloride diffusion coefficient (D_{app}) of control concrete to that of concrete containing NaNO_2 , and DHP are 2.20, and 2.04 respectively for OPC regardless of w/c, and cation type and concentration of chloride salt in the chloride exposure solutions. Similarly, for PPC, the average ratios of D_{app} of control concrete to that of concrete containing NaNO_2 , and DHP are 1.82, and 1.80 respectively.

➤ In case of exposure to composite chloride-sulfate solutions, for OPC, the average ratios of apparent chloride diffusion coefficient of control concrete to that of concrete containing NaNO_2 , and DHP are 1.42, and 1.34 respectively irrespective of w/c, and cation type of chloride salt in the exposure solutions. Similarly, for PPC, the average ratios of D_{app} of control concrete to that containing NaNO_2 , and DHP are 1.06, and 1.10 respectively.

➤ The concrete admixed with DHP mostly showed higher apparent chloride diffusion coefficient as compared to that admixed with NaNO_2 in case of exposure to chloride as well as composite chloride-sulfate solutions.

➤ For both chloride and composite chloride-sulfate solutions, PPC concrete showed higher free chloride content than OPC concrete at lower depth intervals from the exposure surface whereas the opposite variation in free chloride content was observed between OPC and PPC at higher depth intervals from the exposure surface of concrete admixed with and without NaNO_2 , and DHP.

- Between cement type, OPC concrete exhibited higher chloride diffusion coefficient as compared to PPC concrete regardless of presence of corrosion inhibitors, w/c, and cation type of chloride salt in both chloride, and composite chloride-sulfate solutions.
- The free chloride content as well as the apparent chloride diffusion coefficient of both OPC and PPC concrete increased with increase in concentration of chloride salt in the chloride exposure solutions.
- The free chloride ion content and apparent chloride diffusion coefficient (D_{app}) of control concrete were lower in case of exposure to composite chloride-sulfate solutions as compared to chloride solutions. However, in the presence of corrosion inhibitors in concrete, the opposite variation was observed in free chloride content, and D_{app} between chloride and composite chloride-sulfate solutions.
- The cation type associated with chloride ions influenced the chloride binding capacity (R) of concrete. The chloride binding capacity (R) of concrete admixed with and without corrosion inhibitors, and exposed to chloride salt solutions decreased in the order of R: $\text{CaCl}_2 > \text{MgCl}_2 > \text{NaCl}$. Similarly, in case of exposure to composite chloride-sulfate solutions, the chloride binding capacity of concrete decreased in the order of R: $\text{NaCl} + \text{MgSO}_4 > \text{MgCl}_2 + \text{MgSO}_4 > \text{CaCl}_2 + \text{MgSO}_4$.
- The chloride binding capacity of concrete containing DHP was higher than that containing NaNO_2 for both OPC and PPC irrespective of chloride salt in the chloride exposure solutions. However, in case of exposure to composite chloride-sulfate solutions, concrete containing NaNO_2 showed higher chloride binding capacity than DHP.
- The presence of MgSO_4 in the composite chloride-sulfate solution reduced the chloride binding capacity of concrete as compared to that exposed to only chloride solutions irrespective of cation type of chloride salt in the exposure solutions.
- The variations in chloride binding capacity of concrete with cation type of chloride salt in chloride and composite chloride-sulfate exposure solutions, and corrosion inhibitors are in line with the variations in the formations of calcium chloroaluminate as observed from the XRD analysis.
- The higher chloride binding capacity as well as more formation of calcium chloroaluminate as evident from XRD analysis was observed in the concrete exposed to chloride solution of 3.5 % concentration as compared to 1.5%, and 5.5% concentrations for all chloride salts.

- In case of exposure to chloride solutions, the amount of calcium hydroxide, calcium chloroaluminate, and ettringite in the concrete as indicated by the XRD analysis increased with increase in w/c for both cements and corrosion inhibitors.
- For chloride exposure solutions, the amount of calcium hydroxide, and calcium chloroaluminate as observed from the XRD analysis were higher in the depth interval of 5-10 mm from the exposure surface of concrete as compared to other depth intervals.
- The strength of Si-O band as observed from the FTIR spectra was slightly lower in the concrete exposed to $\text{MgCl}_2 + \text{MgSO}_4$ solution as compared to $\text{NaCl} + \text{MgSO}_4$ and $\text{CaCl}_2 + \text{MgSO}_4$ solutions thereby indicating comparatively higher decomposition of C-S-H due to MgSO_4 attack in the concrete subjected to $\text{MgCl}_2 + \text{MgSO}_4$ solution as compared to other composite chloride-sulfate solutions.
- The FESEM images indicated the formation of higher amount of C-S-H in PPC concrete thereby resulting in compacted microstructure as compared to that in OPC concrete.

8.7 Significance of research outcome from the present research work

The durability issues of reinforced concrete have become a serious concern for both scientists, and engineers in the construction industry. It is a well-known fact that the chloride-induced corrosion of steel reinforcement is the most severe durability problem that significantly affects the service life and safety of reinforced concrete structures exposed to severe environmental conditions. In the present study, the influence of cation type of chloride salts, corrosion inhibitors, and mix parameters on chloride ingress, chloride binding, and corrosion of steel reinforcement in concrete exposed to internal chloride, and external chloride and composite chloride-sulfate solutions were evaluated. In addition, the effect of above parameters on variations in microstructure of concrete was also investigated.

The research outcome obtained from the present investigation provided significant information about the effects of cation type of chloride salts, mix parameters, and exposure environment on the performance of nitrite and phosphate based corrosion inhibitors with respect to diffusion of chloride ions, chloride binding, and corrosion of steel reinforcement in concrete. The outcome of the present research work signifies the necessity of use of corrosion inhibitors in concrete due to: a) enhancement of the resistance of concrete against penetration of aggressive ions from service environment, b) improvement in binding of chloride ions in concrete, and c) significant reduction in the extent of corrosion of steel reinforcement. The obtained research findings from the present study suggested that the

corrosion inhibitors used in this investigation, i.e., sodium nitrite (NaNO_2), and di-Sodium hydrogen phosphate (DHP) effectively protected the steel reinforcement against corrosion in two ways i.e., i) through formation of passive layer over steel reinforcement, and ii) by formation of compounds that can block the concrete pores thereby minimizing the ingress of aggressive ions. The outcome from the present research work indicated that sodium nitrite is comparatively more effective in inhibiting corrosion of steel reinforcement as compared to di-Sodium hydrogen phosphate. Nevertheless, di-Sodium hydrogen phosphate (DHP) can be used as a good alternative to sodium nitrite against corrosion of steel reinforcement in concrete as DHP minimized the corrosion activity as compared to control concrete as well as exhibited higher extent of chloride binding as compared to sodium nitrite.

The obtained results indicated that in case of external exposure, even though there is higher chloride binding in OPC concrete, PPC concrete exhibited higher resistance against penetration of chloride ions and reduced the extent of corrosion of steel reinforcement as compared to OPC concrete. In case of internal chloride exposure, OPC showed higher resistance against steel reinforcement corrosion than PPC. Therefore, keeping in view these findings from the present study, for the production of concrete, OPC can be recommended for internal chloride exposure, whereas PPC can be recommended for external chloride exposure environment. The outcome from the present research work indicated that both nitrite and phosphate based corrosion inhibitors i.e., sodium nitrite and di-Sodium hydrogen phosphate are more effective in minimizing the steel reinforcement corrosion in OPC concrete as compared to PPC concrete. In PPC concrete, the formation of denser microstructure is more dominant in minimizing the extent of corrosion of steel reinforcement over the effect of corrosion inhibitors.

The outcome of present investigation showed that sodium chloride (NaCl) is the most aggressive chloride salt as compared to other chloride salts used in this investigation for both internal as well as external chloride exposure conditions. Thus, in case of exposure of concrete structures to chloride environment, the protection measures against corrosion of steel reinforcement need to be adopted while taking into account the detrimental effect of sodium chloride. The obtained results also indicated that the presence of sulfate ions in the exposure solution hinders the ingress of chloride ions whereas it reduces the chloride binding capacity of concrete exposed to external environment. The findings of the present study will be significantly useful in understanding the microstructural changes in concrete

admixed with corrosion inhibitors and exposed to external solutions of different chloride salts. Further, the corroboration of variations in chloride binding capacity with that in the formation of different compounds in concrete as observed from the microstructure analysis provides information about the variations in the interaction of chloride ions with cement hydration products in the presence of corrosion inhibitors in concrete.

8.8 Suggestions for further study

Following are the suggestions for further work:

- The present research work can be extended to evaluate the effect of mineral admixtures namely fly ash, ground granulated blast furnace slag, silica fume, etc. on chloride ingress, chloride binding, microstructure, and steel reinforcement corrosion in concrete containing corrosion inhibitors and exposed to chloride, and composite chloride-sulfate environment.
- The present study can also be extended to evaluate the effectiveness of other types of corrosion inhibitors in concrete exposed to chloride and composite chloride-sulfate solutions.
- In addition, there is a great scope to study the effect of cation type associated with chloride ions, and corrosion inhibitors on steel reinforcement corrosion in geopolymer concrete.

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Appendix A

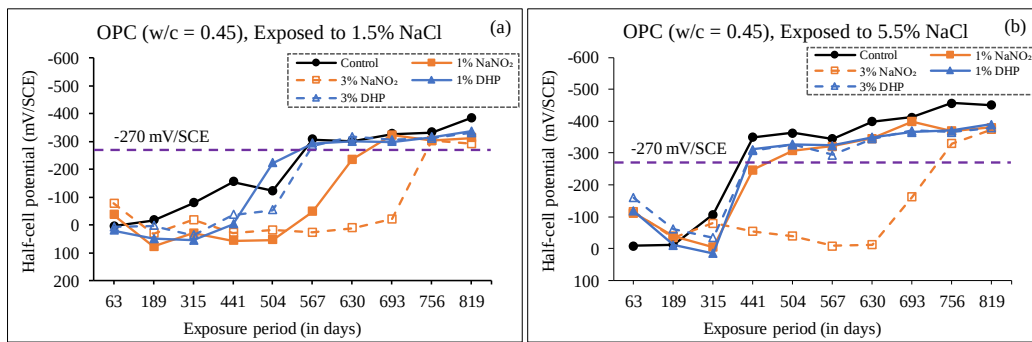


Fig. A1 Half-cell potential (E_0) of steel reinforcement in OPC concrete at w/c 0.45, and exposed to different concentrations of NaCl solution: (a) 1.5%, and (b) 5.5%

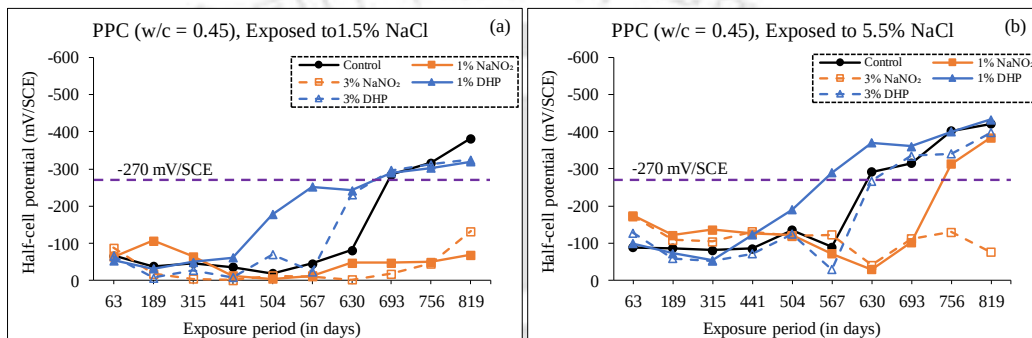


Fig. A2 Half-cell potential (E_0) of steel reinforcement in PPC concrete at w/c 0.45, and exposed to different concentrations of NaCl solution: (a) 1.5%, and (b) 5.5%

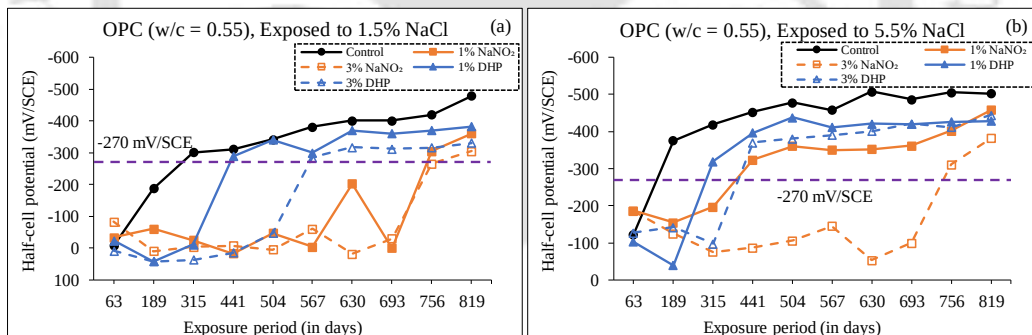


Fig. A3 Half-cell potential (E_0) of steel reinforcement in OPC concrete at w/c 0.55, and exposed to different concentrations of NaCl solution: (a) 1.5%, and (b) 5.5%

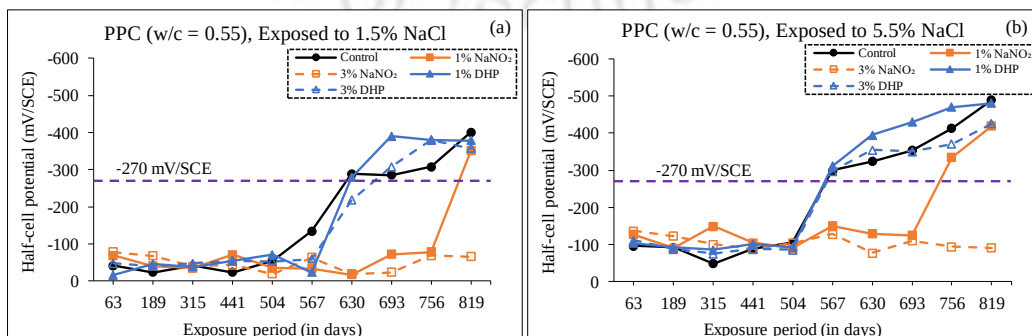


Fig. A4 Half-cell potential (E_0) of steel reinforcement in PPC concrete at w/c 0.55, and exposed to different concentrations of NaCl solution: (a) 1.5%, and (b) 5.5%

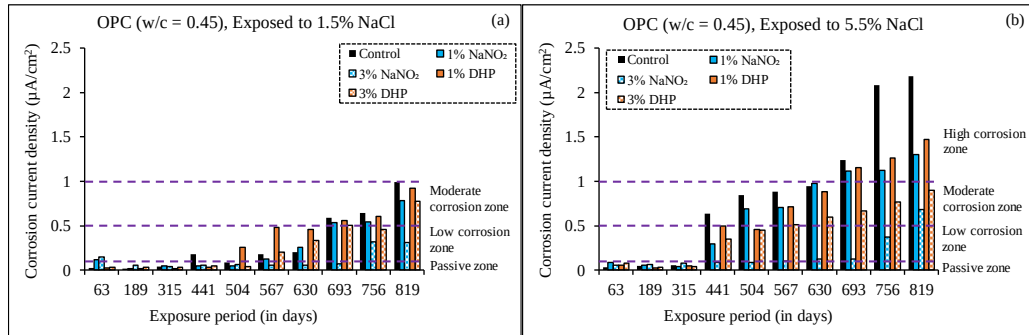


Fig. A5 Corrosion current density (I_{corr}) of steel reinforcement in OPC concrete at w/c 0.45, and exposed to different concentrations of NaCl solution: (a) 1.5%, and (b) 5.5%

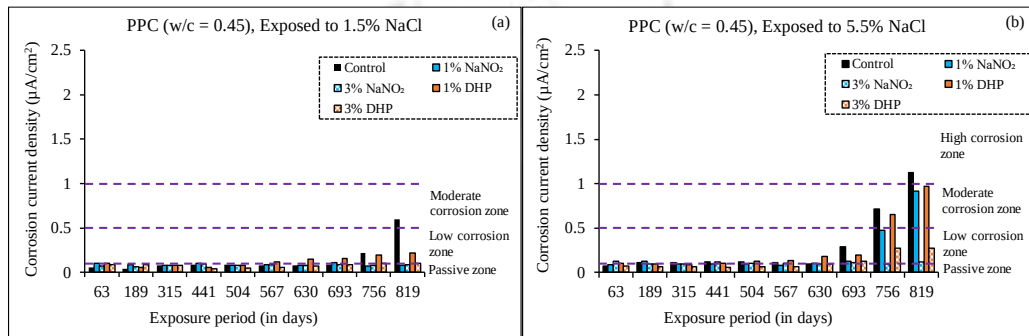


Fig. A6 Corrosion current density (I_{corr}) of steel reinforcement in PPC concrete at w/c 0.45, and exposed to different concentrations of NaCl solution: (a) 1.5%, and (b) 5.5%

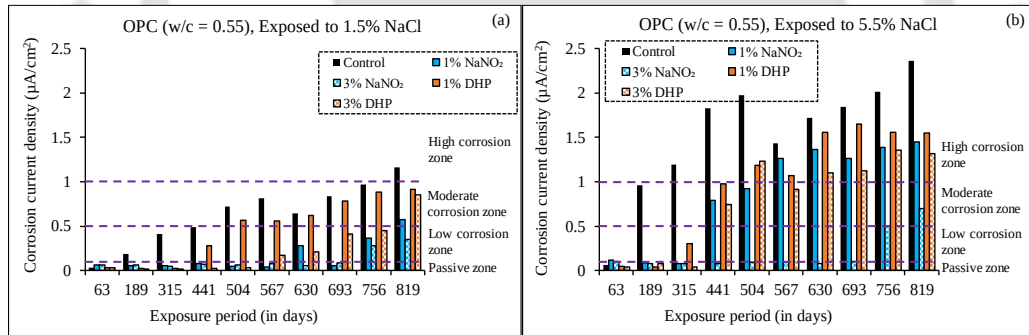


Fig. A7 Corrosion current density (I_{corr}) of steel reinforcement in OPC concrete at w/c 0.55, and exposed to different concentrations of NaCl solution: (a) 1.5%, and (b) 5.5%

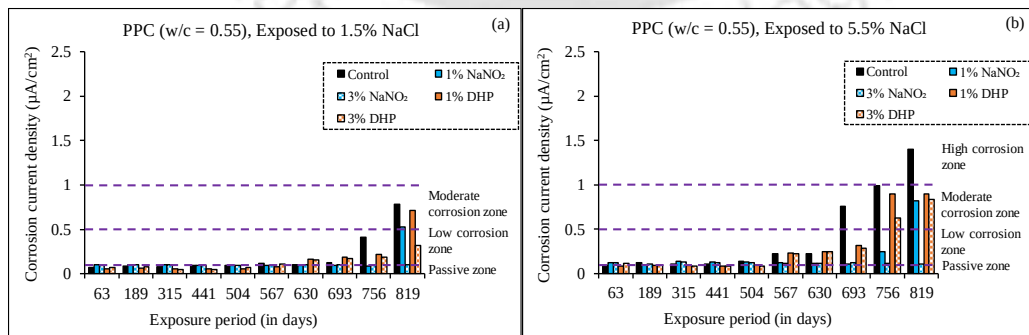


Fig. A8 Corrosion current density (I_{corr}) of steel reinforcement in PPC concrete at w/c 0.55, and exposed to different concentrations of NaCl solution: (a) 1.5%, and (b) 5.5%

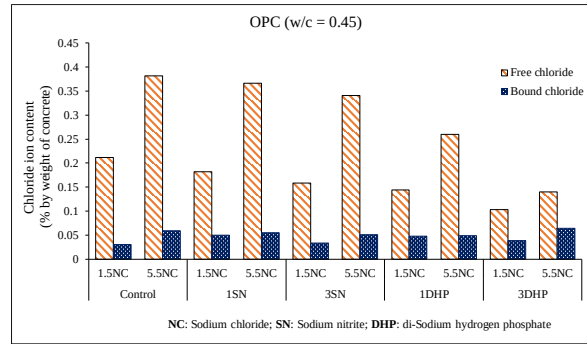


Fig. A9 Free and bound chloride ion contents of OPC control mix and that admixed with corrosion inhibitors at w/c of 0.45, and exposed to 1.5% and 5.5% NaCl solutions

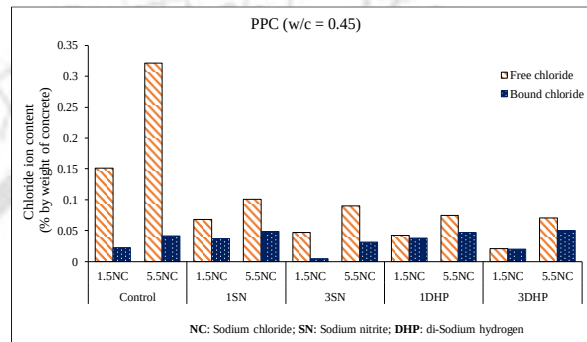


Fig. A10 Free and bound chloride ion contents of PPC control mix and that admixed with corrosion inhibitors at w/c of 0.45, and exposed to 1.5% and 5.5% NaCl solutions

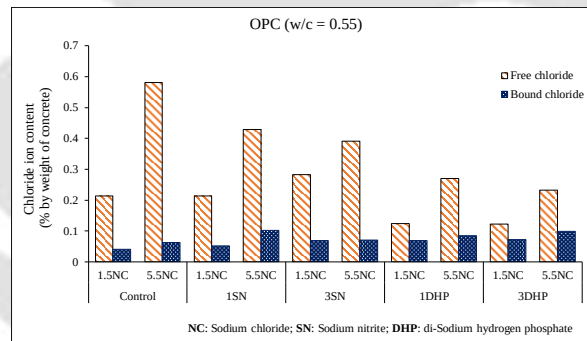


Fig. A11 Free and bound chloride ion contents of OPC control mix and that admixed with corrosion inhibitors at w/c of 0.55, and exposed to 1.5% and 5.5% NaCl solutions

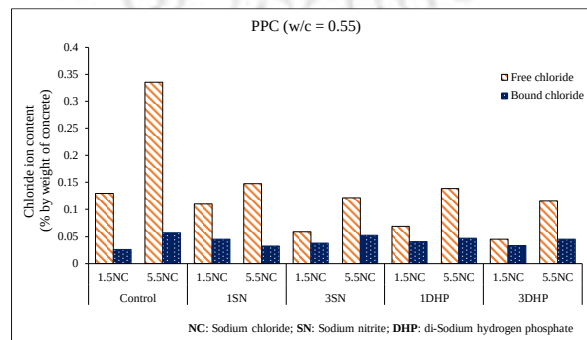


Fig. A12 Free and bound chloride ion contents of PPC control mix and that admixed with corrosion inhibitors at w/c of 0.55, and exposed to 1.5% and 5.5% NaCl solutions

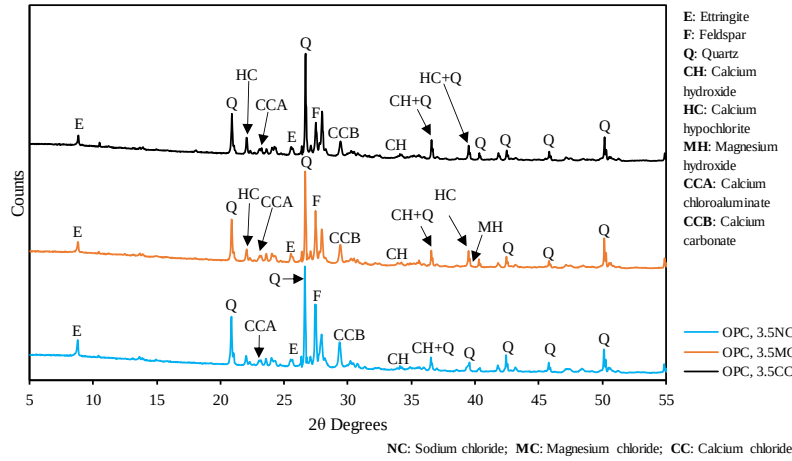


Fig. A13 XRD patterns of control concrete made from OPC at w/c of 0.55, and exposed to different chloride salt solutions

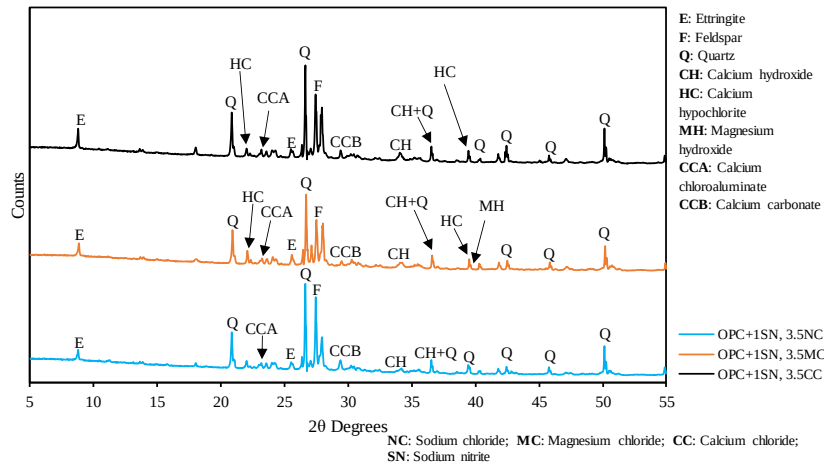


Fig. A14 XRD patterns of OPC concrete admixed with 1% NaNO_2 at w/c of 0.45, and exposed to different chloride salt solutions

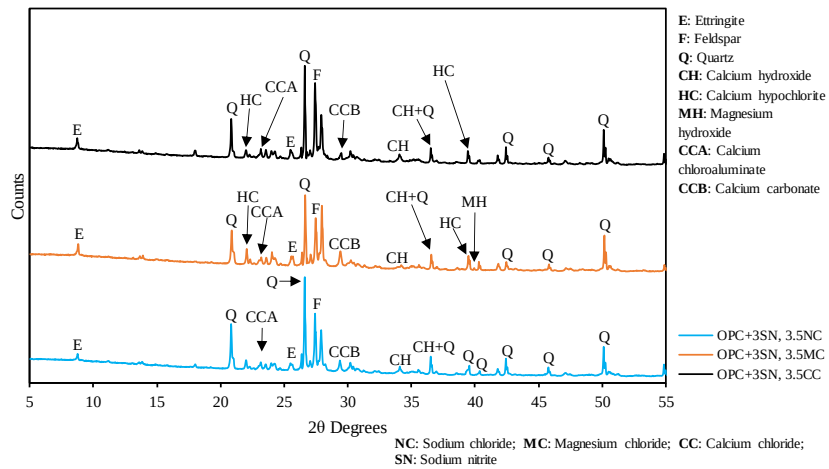


Fig. A15 XRD patterns of OPC concrete admixed with 3% NaNO_2 at w/c of 0.55, and exposed to different chloride salt solutions

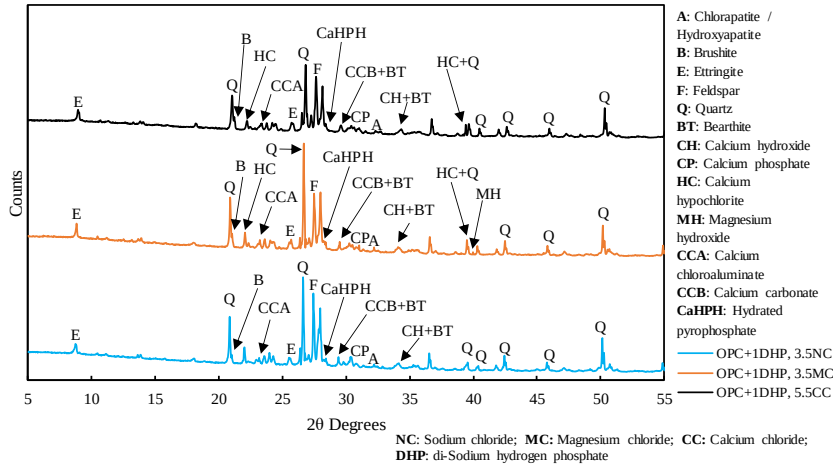


Fig. A16 XRD patterns of OPC concrete admixed with 1% DHP at w/c of 0.55, and exposed to different chloride salt solutions

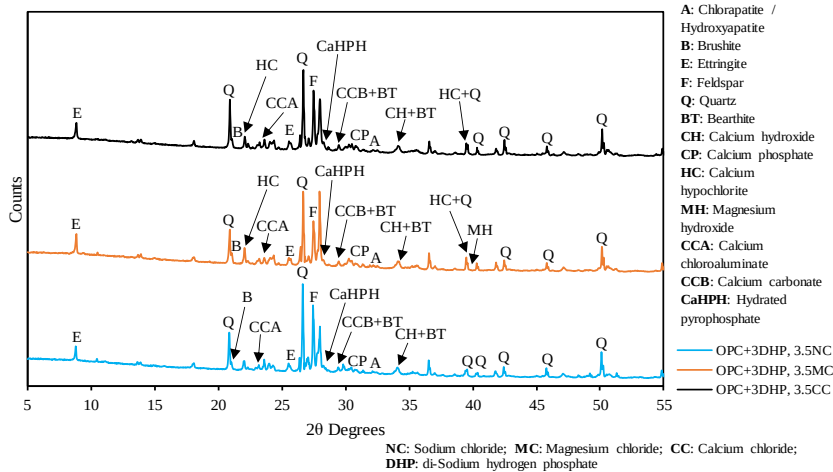


Fig. A17 XRD patterns of OPC concrete admixed with 3% DHP at w/c of 0.45, and exposed to different chloride salt solutions

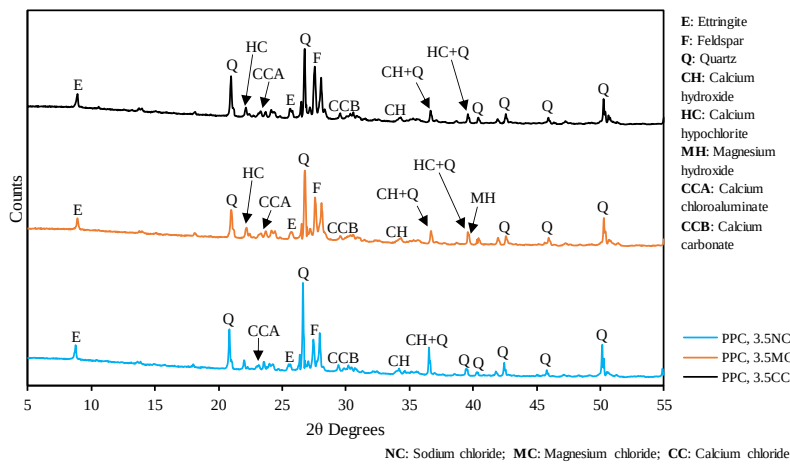


Fig. A18 XRD patterns of control concrete made from PPC at w/c of 0.45, and exposed to different chloride salt solutions

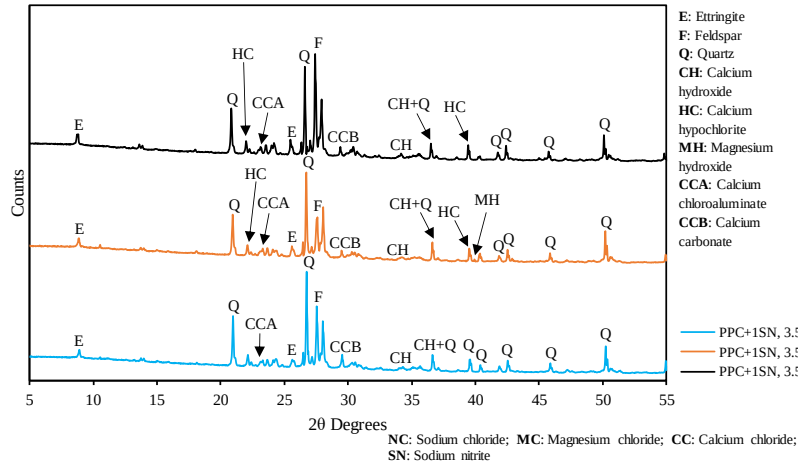


Fig. A19 XRD patterns of PPC concrete admixed with 1% NaNO_2 at w/c of 0.55, and exposed to different chloride salt solutions

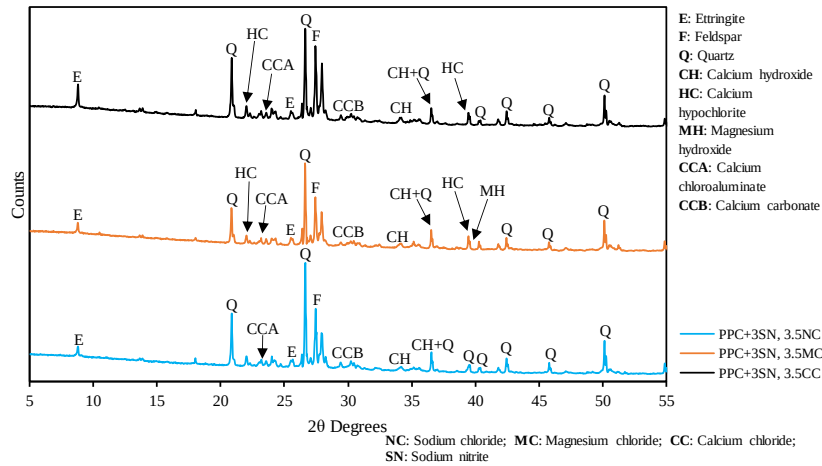


Fig. A20 XRD patterns of PPC concrete admixed with 3% NaNO_2 at w/c of 0.45, and exposed to different chloride salt solutions

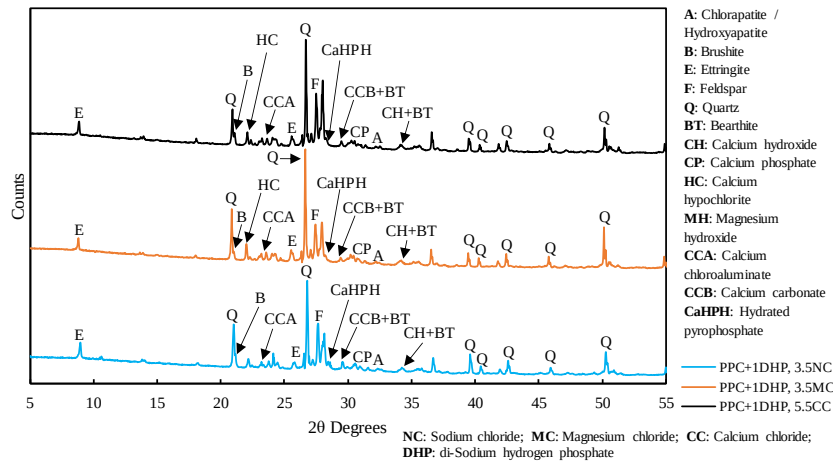


Fig. A21 XRD patterns of PPC concrete admixed with 1% DHP at w/c of 0.45, and exposed to different chloride salt solutions

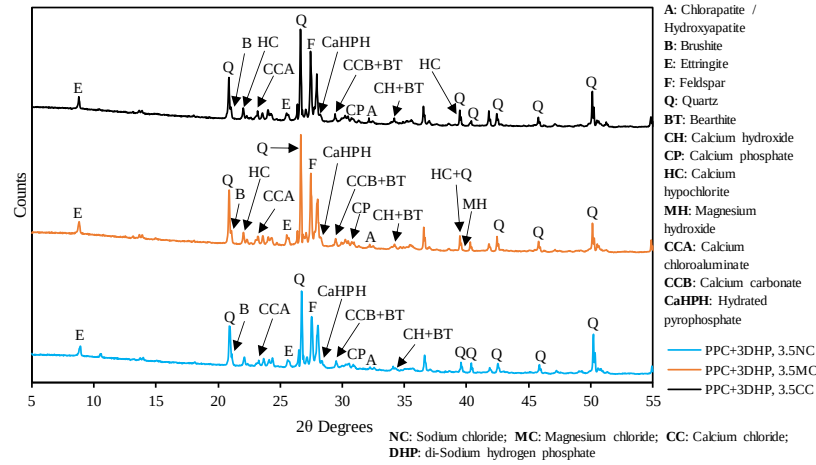


Fig. A22 XRD patterns of PPC concrete admixed with 3% DHP at w/c of 0.55, and exposed to different chloride salt solutions

Appendix B

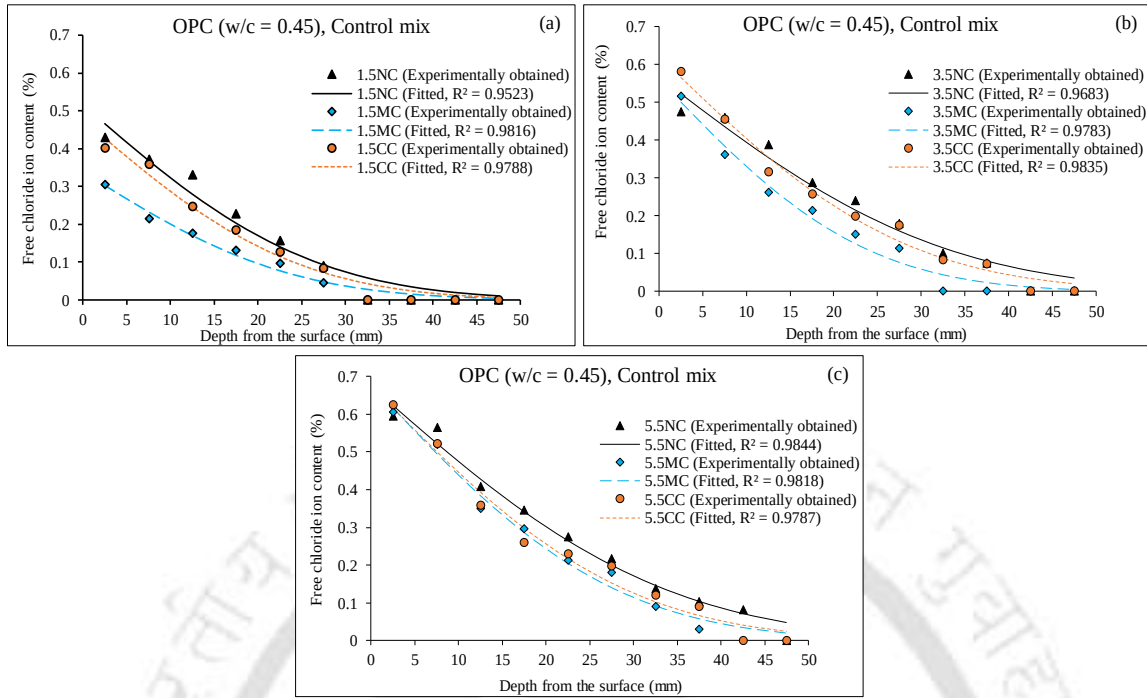


Fig. B1 Experimentally obtained and fitted free chloride ion (C_F) content profile of control concrete made from OPC at w/c of 0.45 and exposed to chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂) of different concentrations: (a) 1.5%, (b) 3.5%, and (c) 5.5%

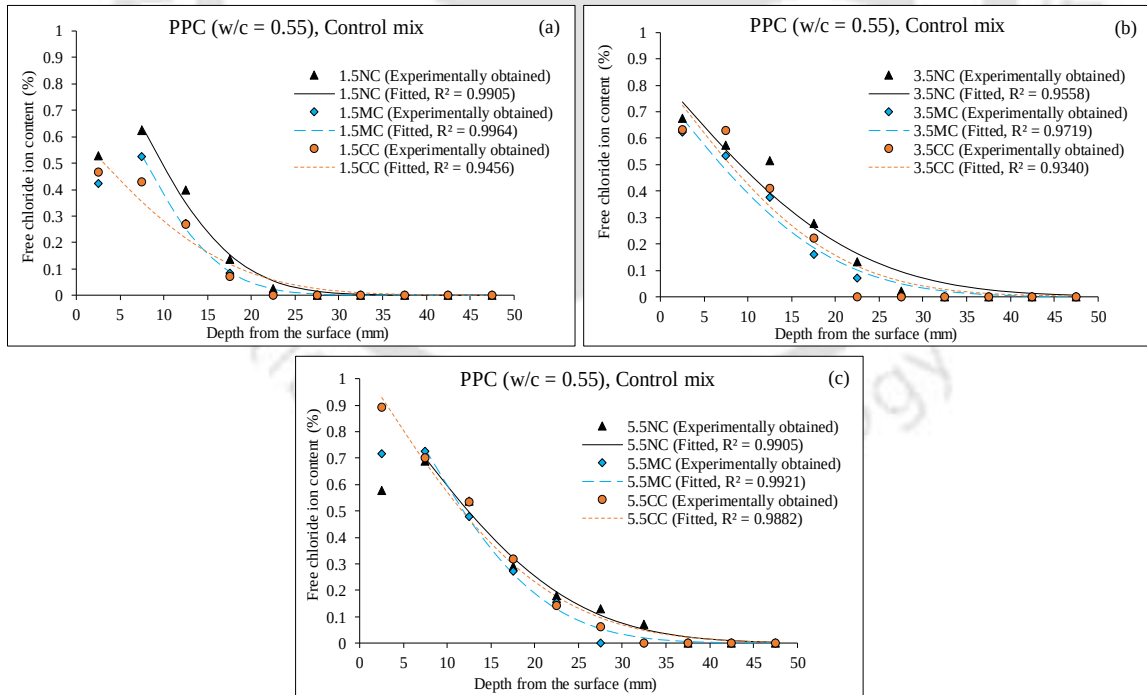


Fig. B2 Experimentally obtained and fitted free chloride ion (C_F) content profile of control concrete made from PPC at w/c of 0.55 and exposed to chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂) of different concentrations: (a) 1.5%, (b) 3.5%, and (c) 5.5%

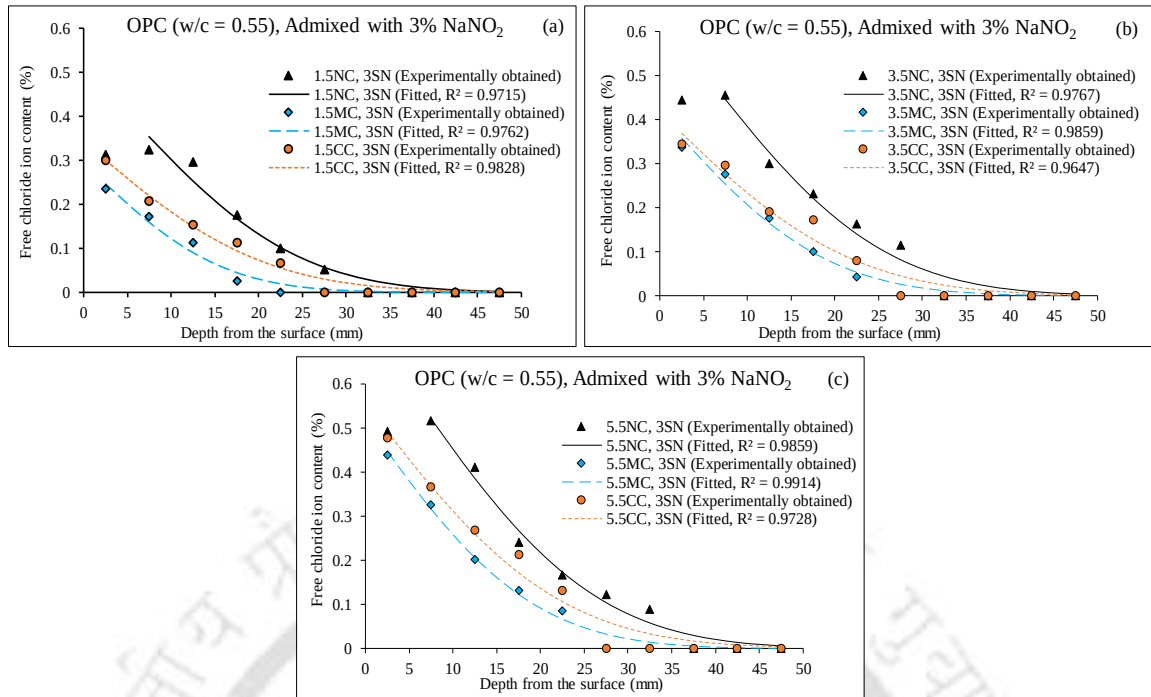


Fig. B3 Experimentally obtained and fitted free chloride ion (C_F) content profile of OPC concrete containing 3% NaNO_2 at w/c of 0.55 and exposed to chloride salt solutions (i.e., NaCl , MgCl_2 , and CaCl_2) of different concentrations: (a) 1.5%, (b) 3.5%, and (c) 5.5%

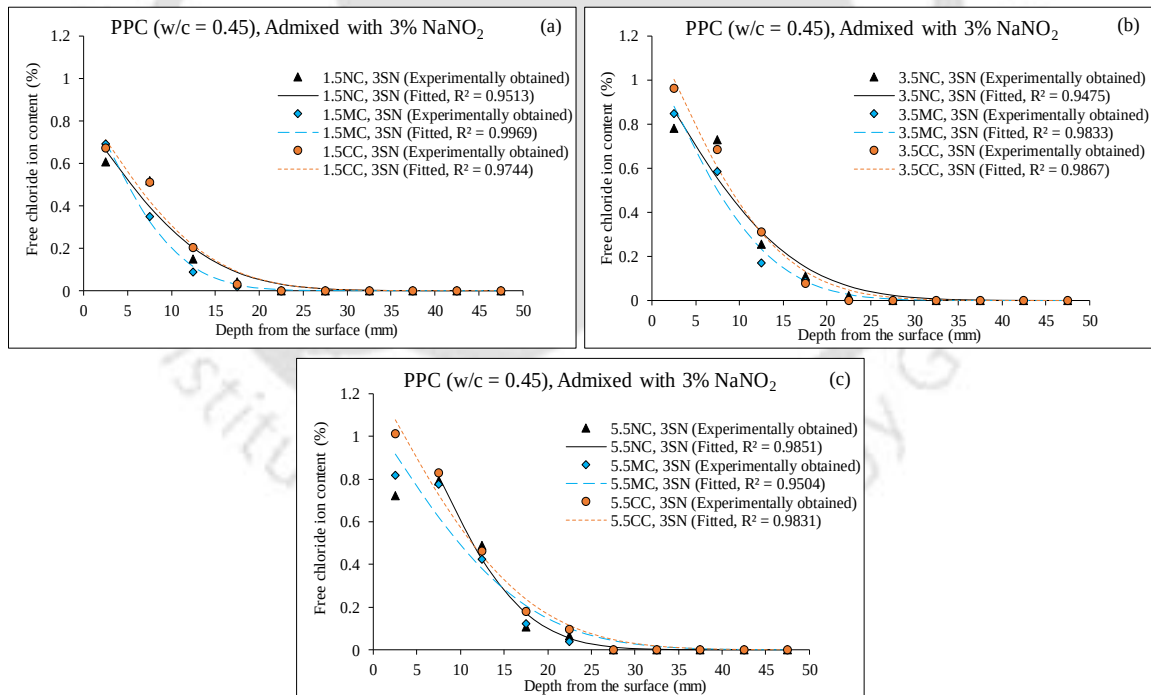


Fig. B4 Experimentally obtained and fitted free chloride ion (C_F) content profile of PPC concrete containing 3% NaNO_2 at w/c of 0.45 and exposed to chloride salt solutions (i.e., NaCl , MgCl_2 , and CaCl_2) of different concentrations: (a) 1.5%, (b) 3.5%, and (c) 5.5%

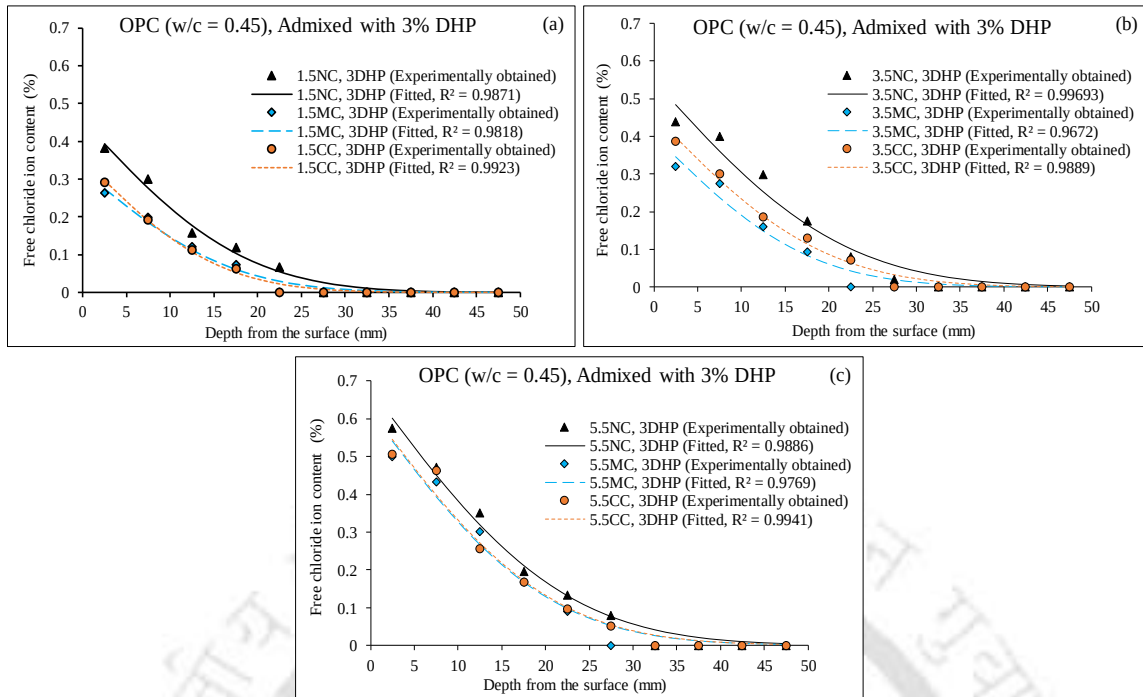


Fig. B5 Experimentally obtained and fitted free chloride ion (C_F) content profile of OPC concrete containing 3% DHP at w/c of 0.45 and exposed to chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂) of different concentrations: (a) 1.5%, (b) 3.5%, and (c) 5.5%

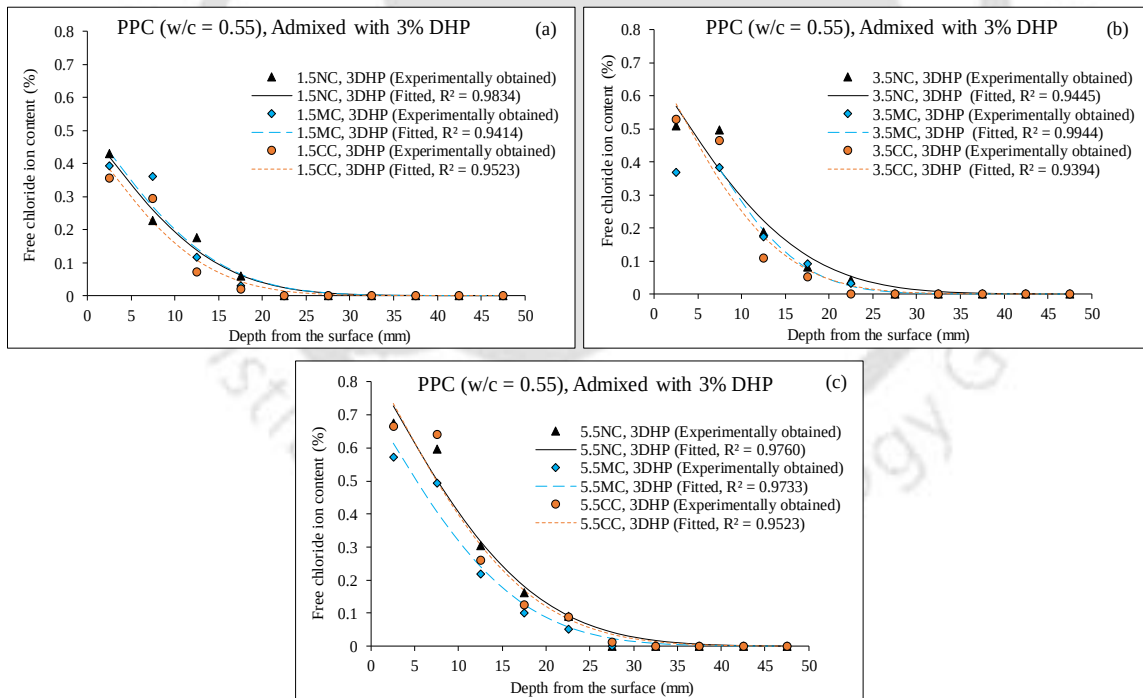


Fig. B6 Experimentally obtained and fitted free chloride ion (C_F) content profile of PPC concrete containing 3% DHP at w/c of 0.55 and exposed to chloride salt solutions (i.e., NaCl, MgCl₂, and CaCl₂) of different concentrations: (a) 1.5%, (b) 3.5%, and (c) 5.5%

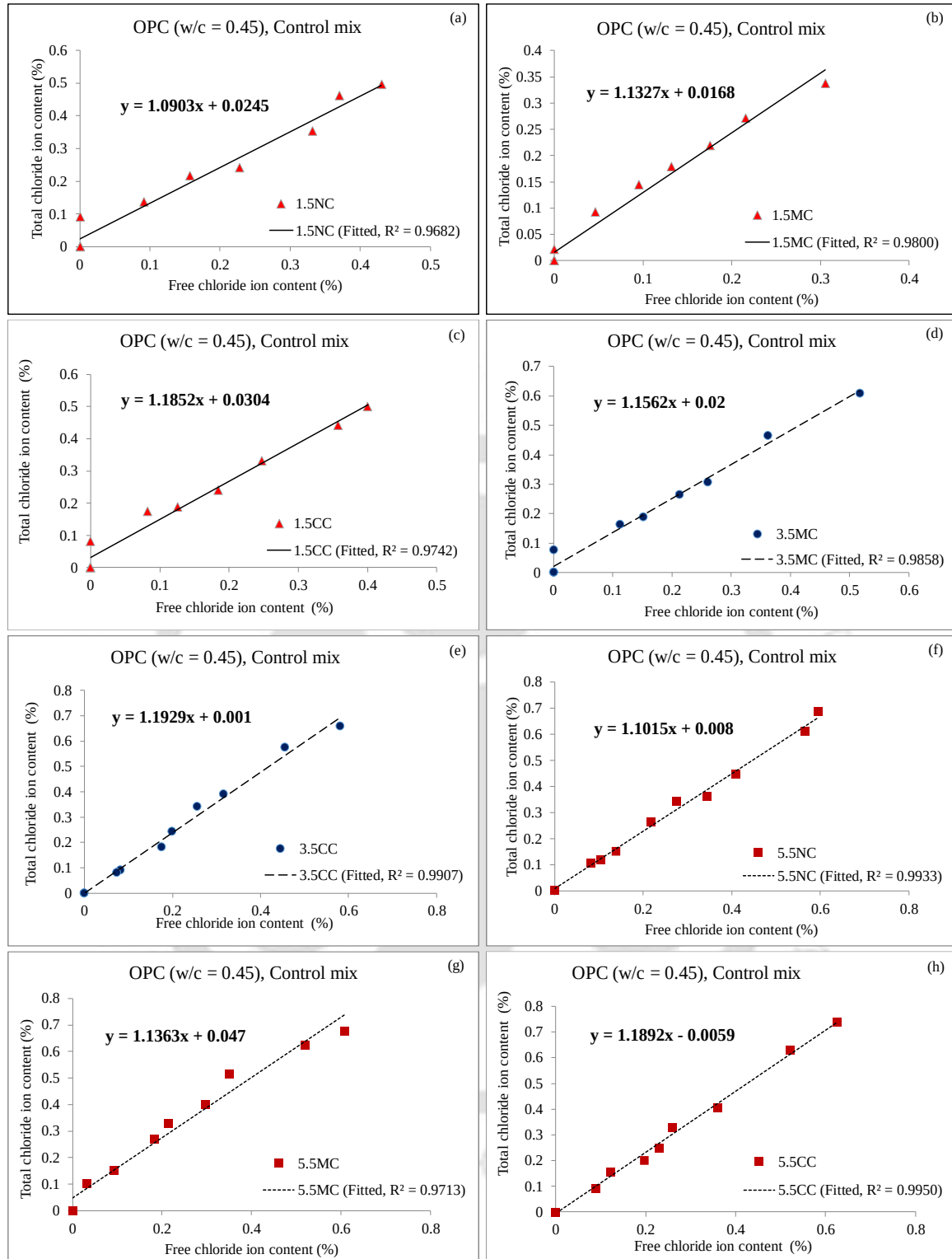


Fig. B7 Relationship between free chloride ion and total chloride ion contents of OPC control concrete (without corrosion inhibitors) at w/c of 0.45 and exposed to chloride salt solutions of different concentrations: (a) 1.5% NaCl, (b) 1.5% $MgCl_2$, (c) 1.5% $CaCl_2$, (d) 3.5% $MgCl_2$, (e) 3.5% $CaCl_2$, (f) 5.5% NaCl, (g) 5.5% $MgCl_2$, and (h) 5.5% $CaCl_2$

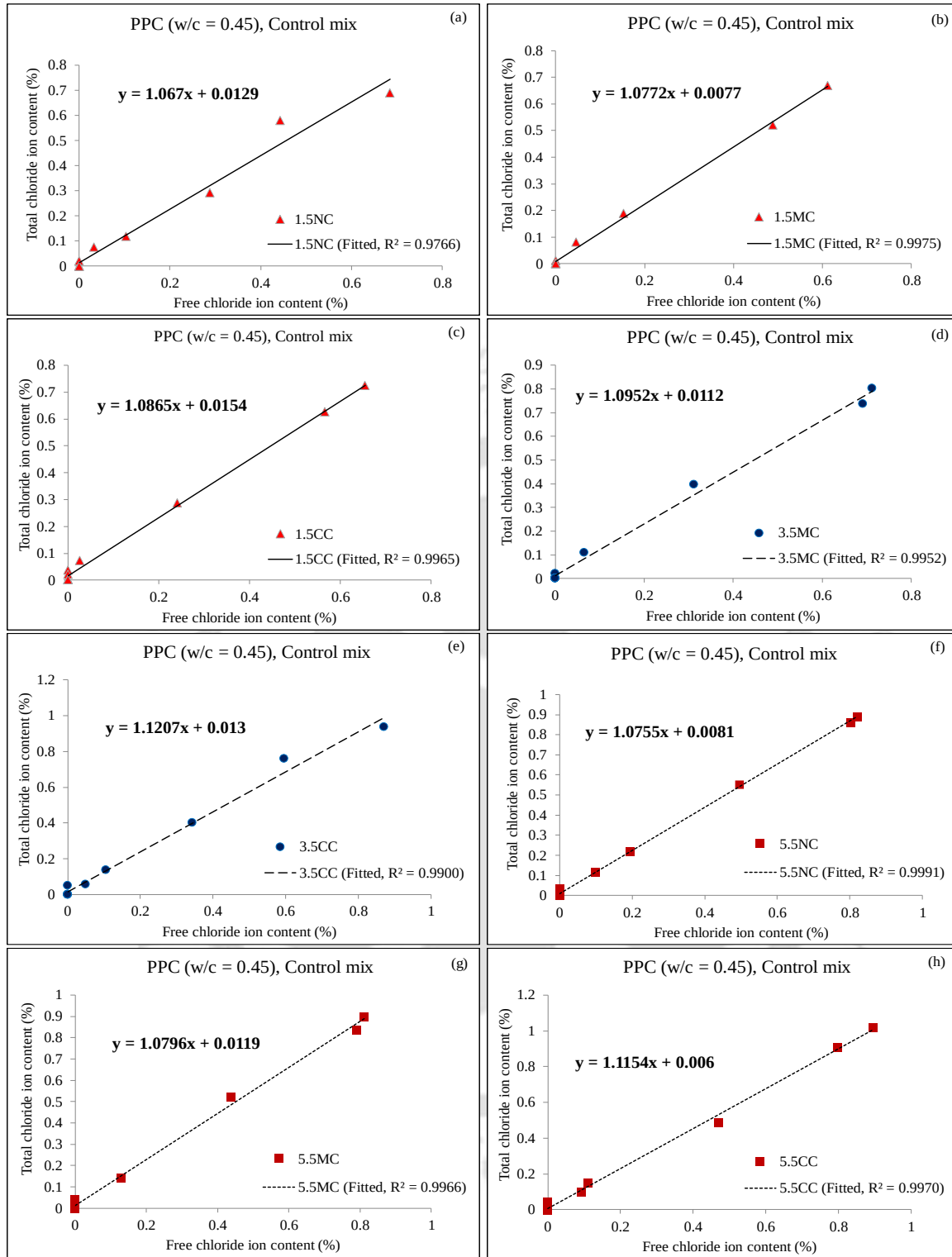
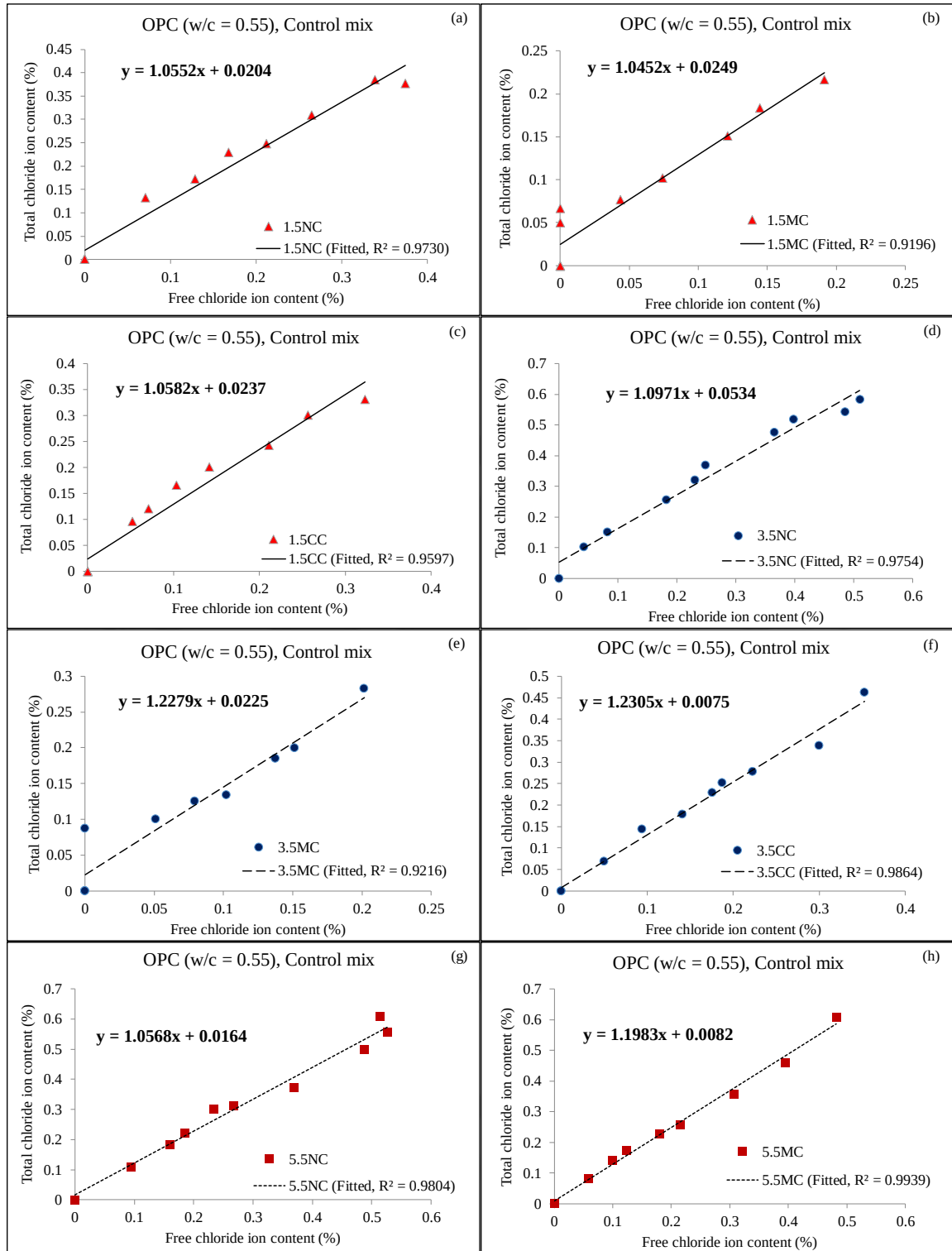


Fig. B8 Relationship between free chloride ion and total chloride ion contents of PPC control concrete (without corrosion inhibitors) at w/c of 0.45 and exposed to chloride salt solutions of different concentrations: (a) 1.5% NaCl, (b) 1.5% $MgCl_2$, (c) 1.5% $CaCl_2$, (d) 3.5% $MgCl_2$, (e) 3.5% $CaCl_2$, (f) 5.5% NaCl, (g) 5.5% $MgCl_2$, and (h) 5.5% $CaCl_2$



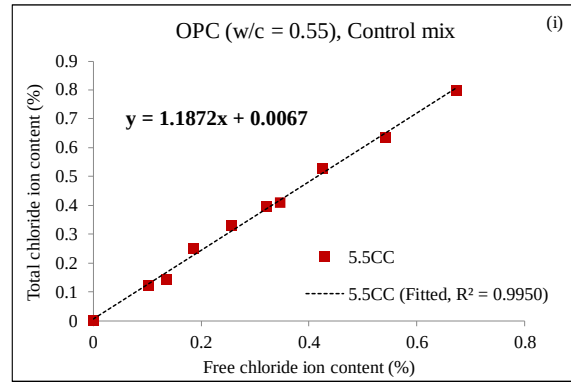
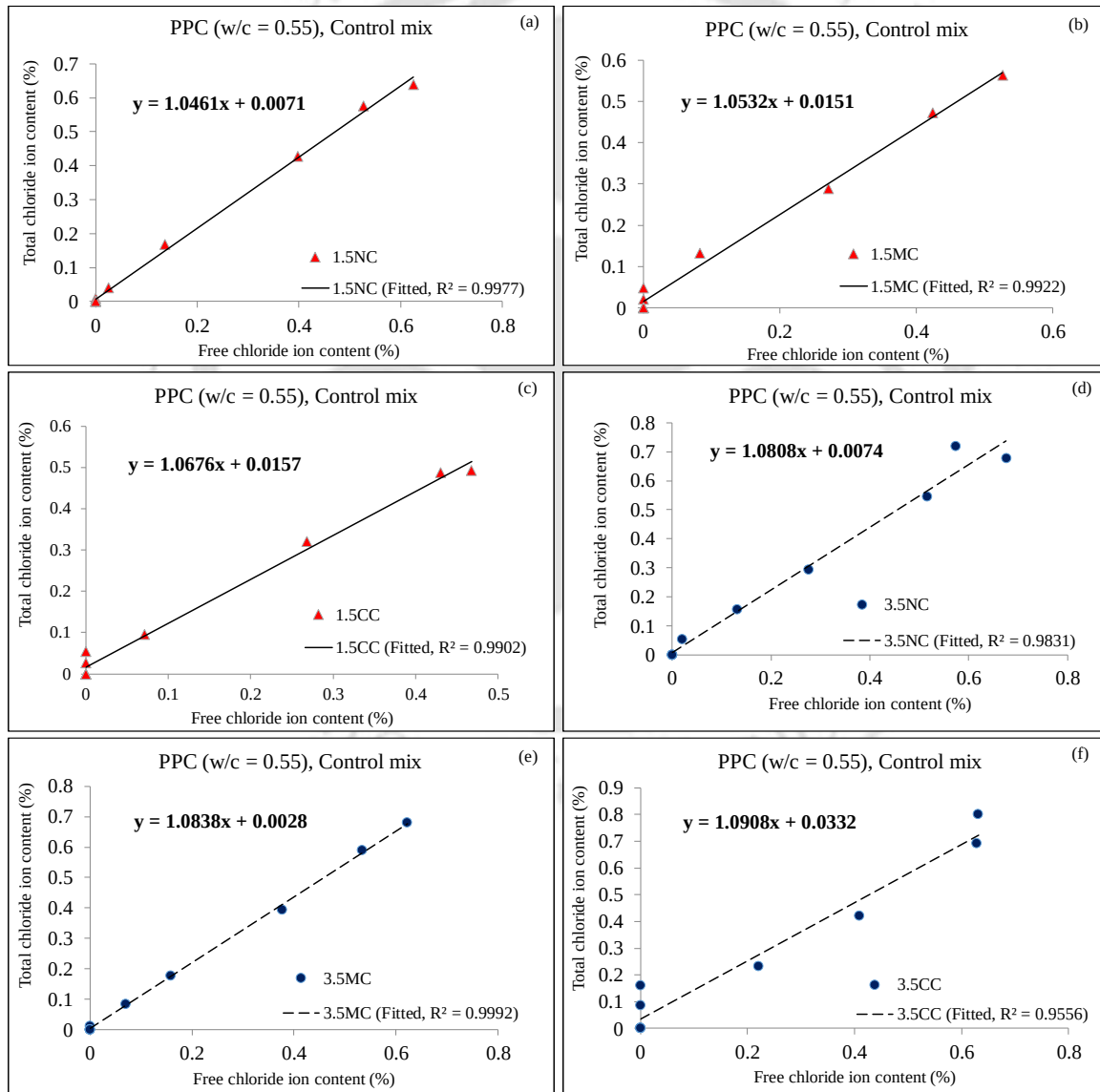


Fig. B9 Relationship between free chloride ion and total chloride ion contents of OPC control concrete (without corrosion inhibitors) at w/c of 0.55 and exposed to chloride salt solutions of different concentrations: (a) 1.5% NaCl, (b) 1.5% MgCl₂, (c) 1.5% CaCl₂, (d) 3.5% NaCl, (e) 3.5% MgCl₂, (f) 3.5% CaCl₂, (g) 5.5% NaCl, (h) 5.5% MgCl₂, and (i) 5.5% CaCl₂



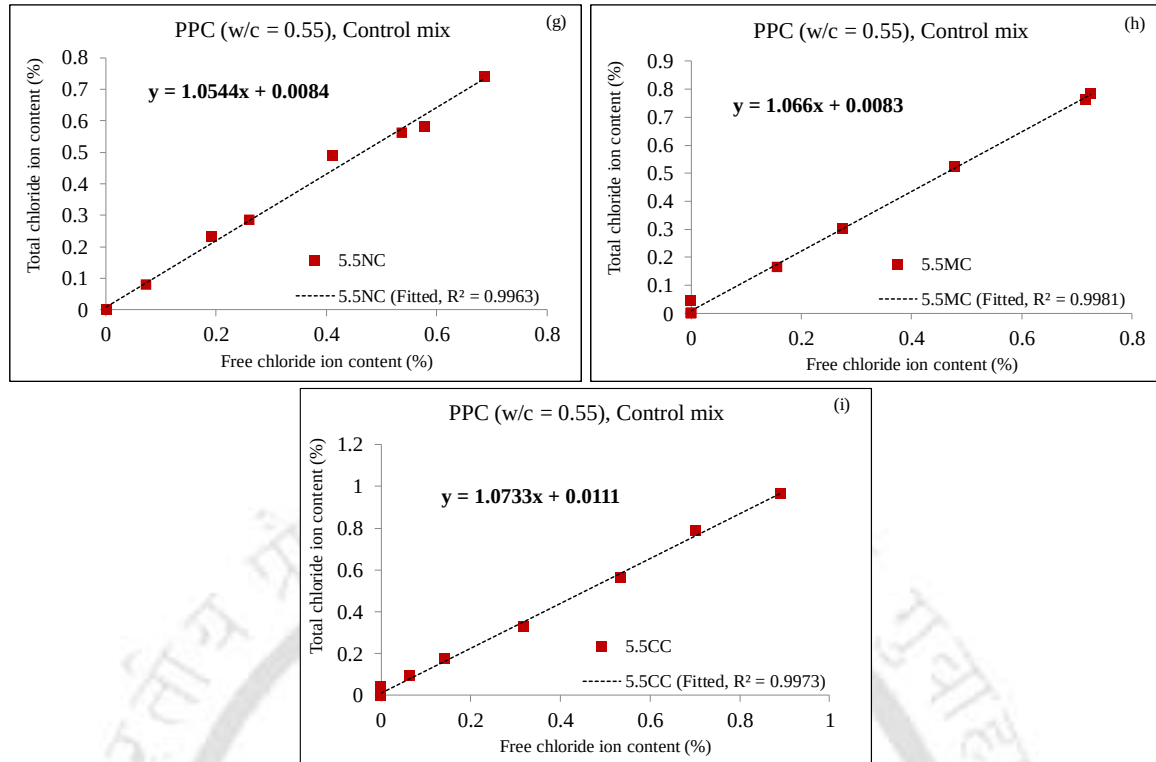
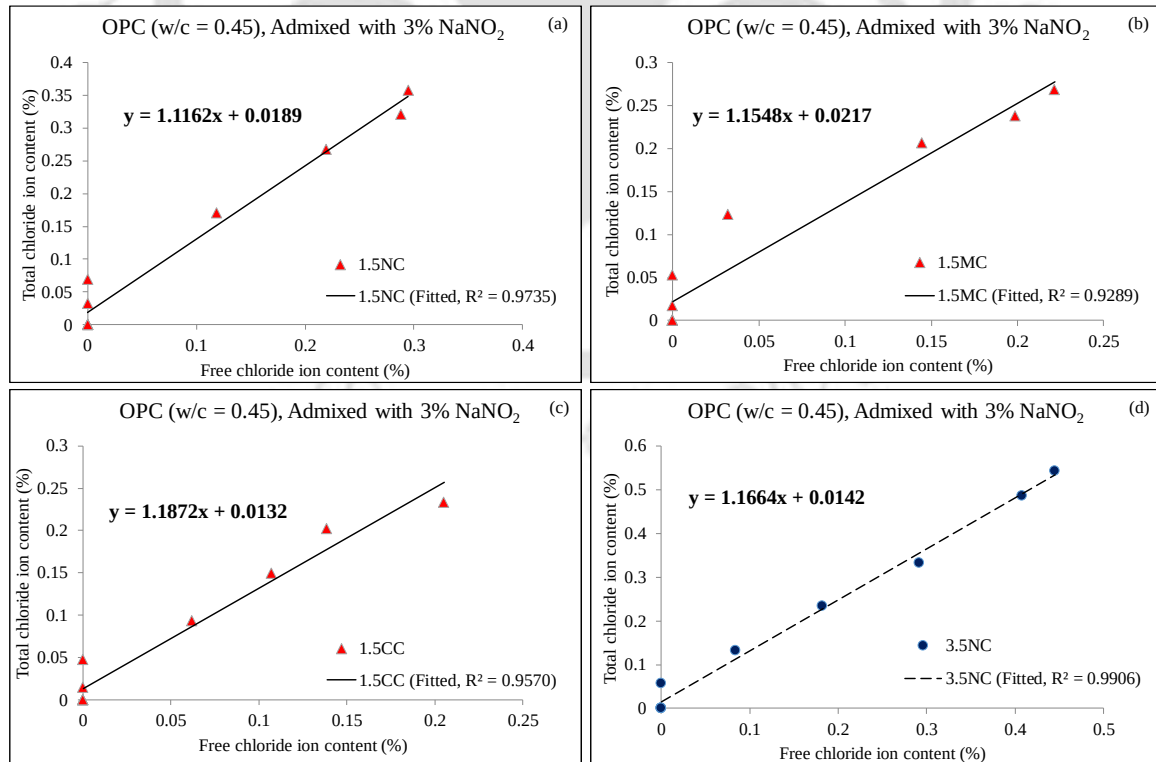


Fig. B10 Relationship between free chloride ion and total chloride ion contents of PPC control concrete (without corrosion inhibitors) at w/c of 0.55 and exposed to chloride salt solutions of different concentrations: (a) 1.5% NaCl, (b) 1.5% MgCl₂, (c) 1.5% CaCl₂, (d) 3.5% NaCl, (e) 3.5% MgCl₂, (f) 3.5% CaCl₂, (g) 5.5% NaCl, (h) 5.5% MgCl₂, and (i) 5.5% CaCl₂



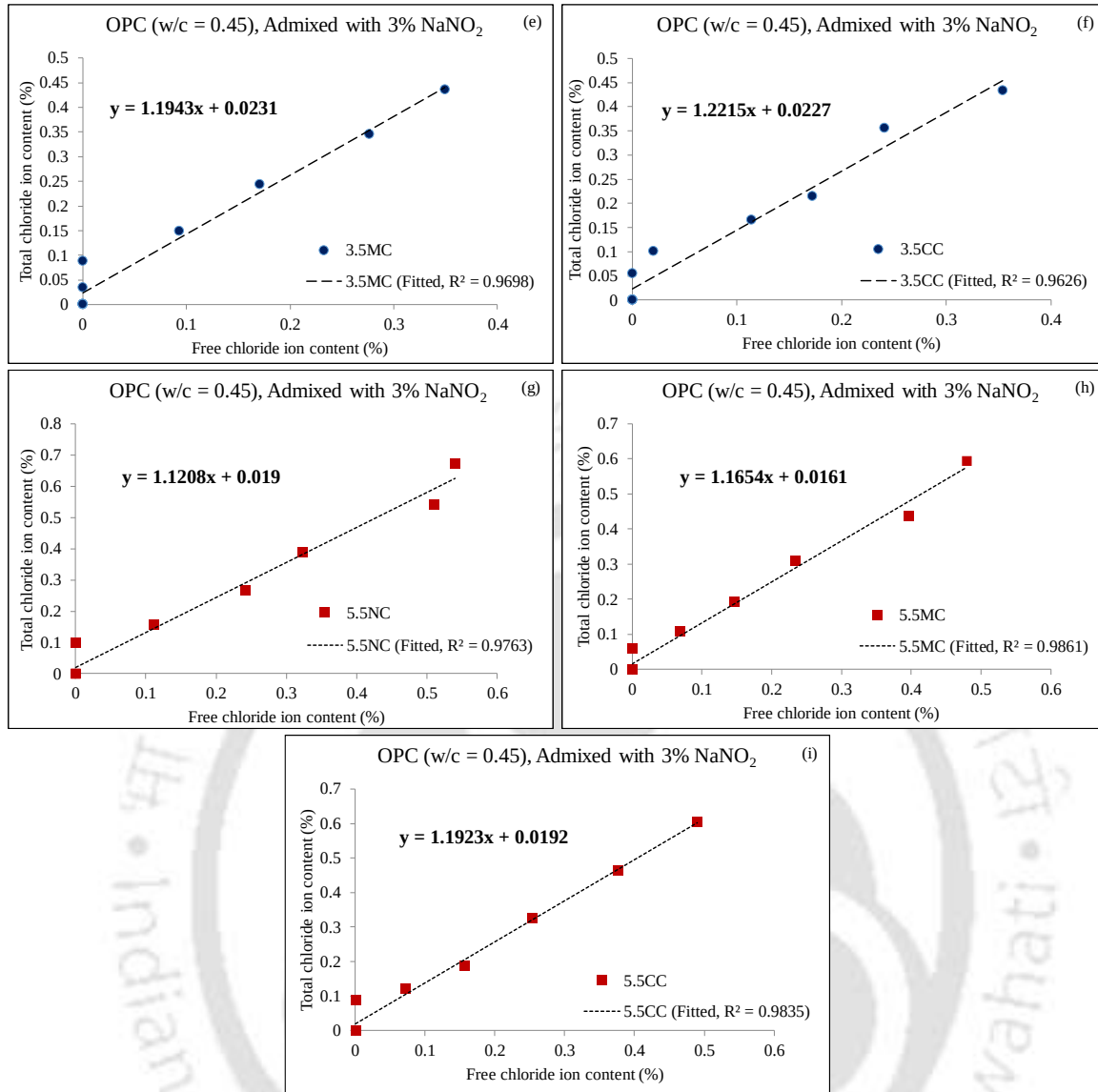
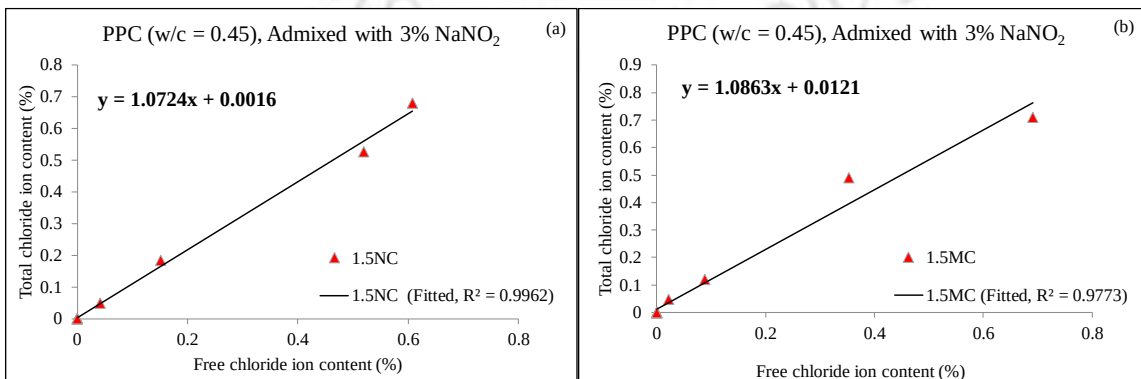


Fig. B11 Relationship between free chloride ion and total chloride ion contents of OPC concrete containing 3% NaNO₂ at w/c of 0.45 and exposed to chloride salt solutions of different concentrations: (a) 1.5% NaCl, (b) 1.5% MgCl₂, (c) 1.5% CaCl₂, (d) 3.5% NaCl, (e) 3.5% MgCl₂, (f) 3.5% CaCl₂, (g) 5.5% NaCl, (h) 5.5% MgCl₂, and (i) 5.5% CaCl₂



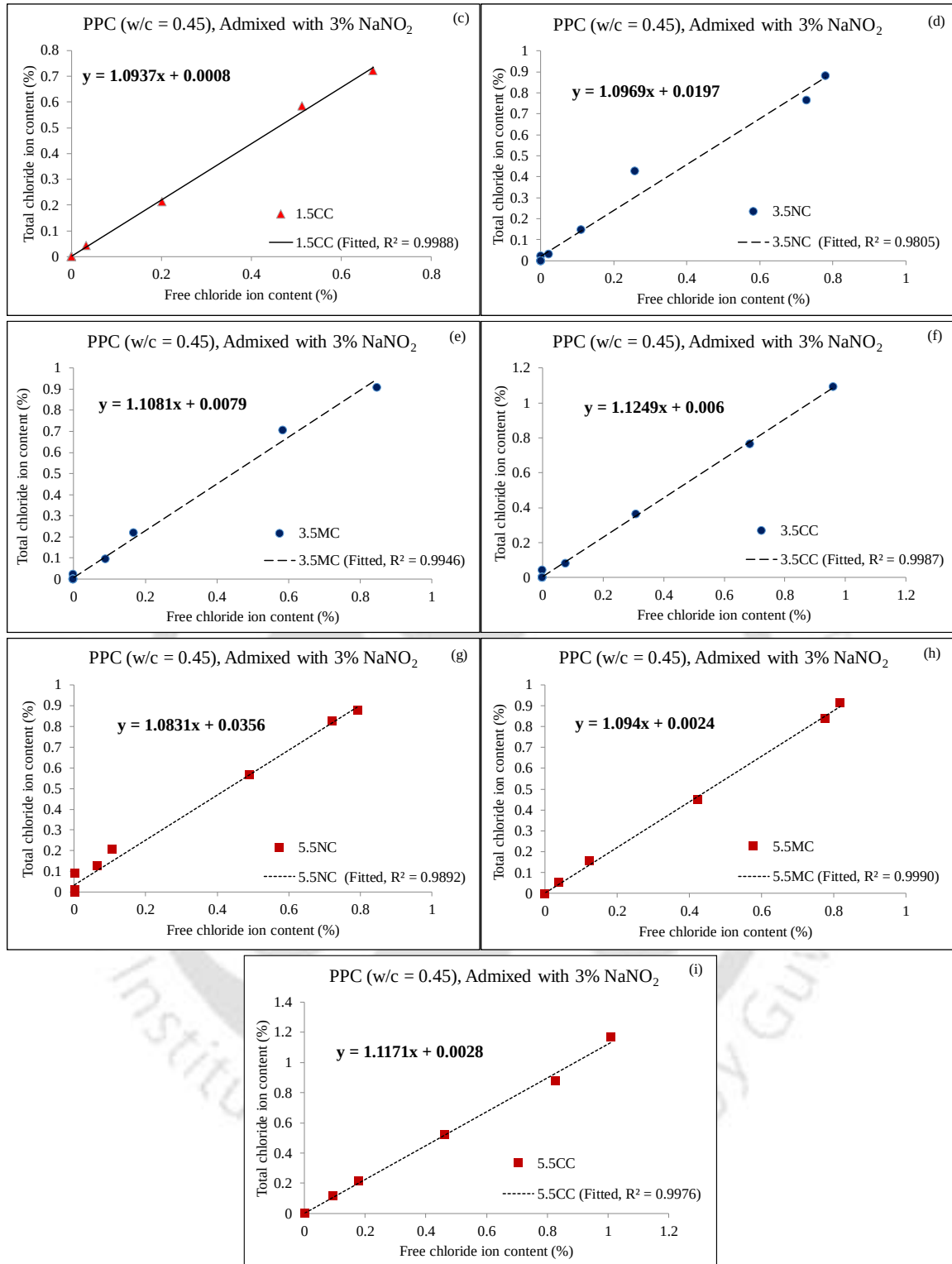


Fig. B12 Relationship between free chloride ion and total chloride ion contents of PPC concrete containing 3% NaNO₂ at w/c of 0.45 and exposed to chloride salt solutions of different concentrations: (a) 1.5% NaCl, (b) 1.5% MgCl₂, (c) 1.5% CaCl₂, (d) 3.5% NaCl, (e) 3.5% MgCl₂, (f) 3.5% CaCl₂, (g) 5.5% NaCl, (h) 5.5% MgCl₂, and (i) 5.5% CaCl₂

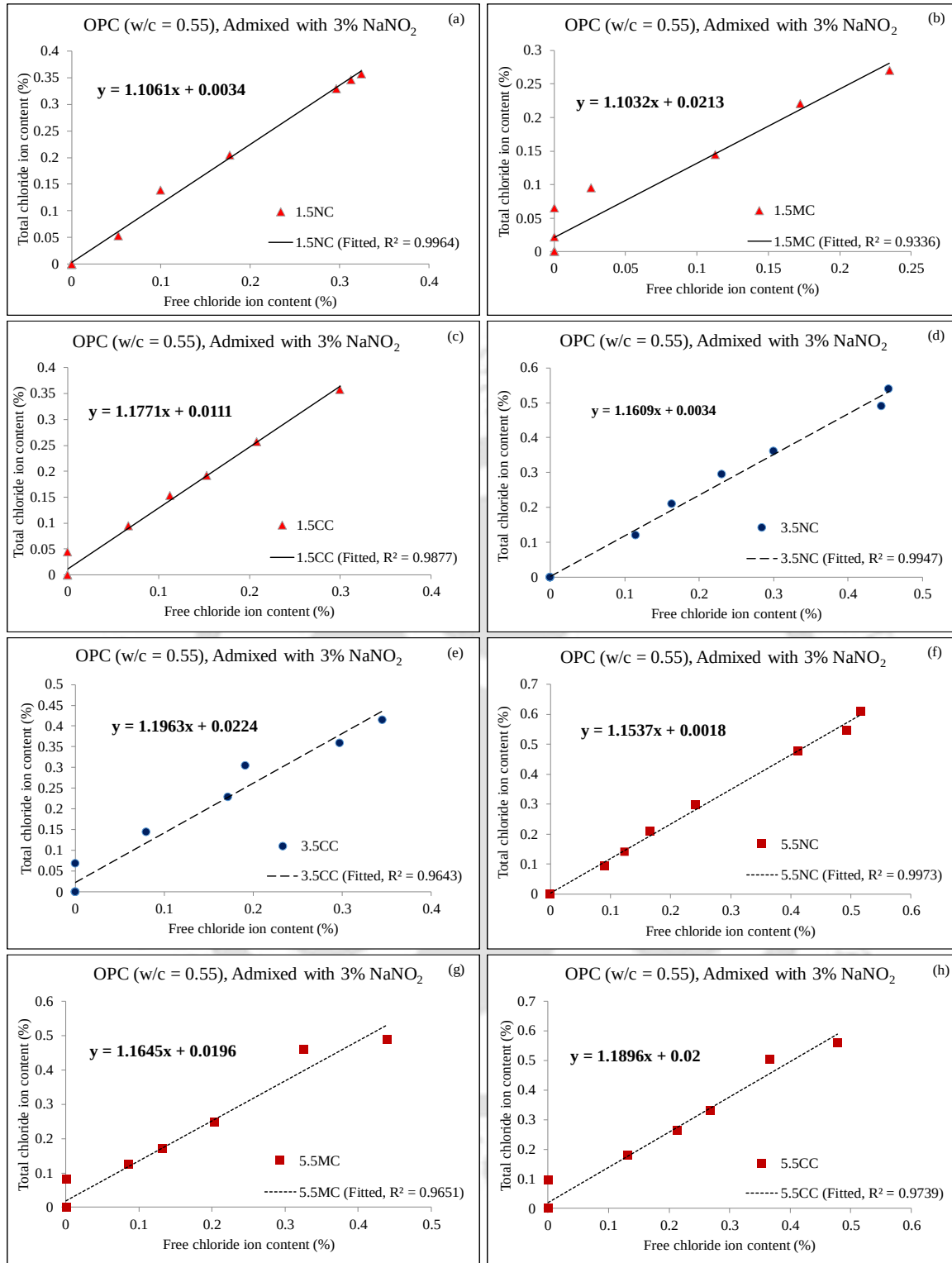


Fig. B13 Relationship between free chloride ion and total chloride ion contents of OPC concrete containing 3% NaNO₂ at w/c of 0.55 and exposed to chloride salt solutions of different concentrations: (a) 1.5% NaCl, (b) 1.5% MgCl₂, (c) 1.5% CaCl₂, (d) 3.5% NaCl, (e) 3.5% CaCl₂, (f) 5.5% NaCl, (g) 5.5% MgCl₂, and (h) 5.5% CaCl₂

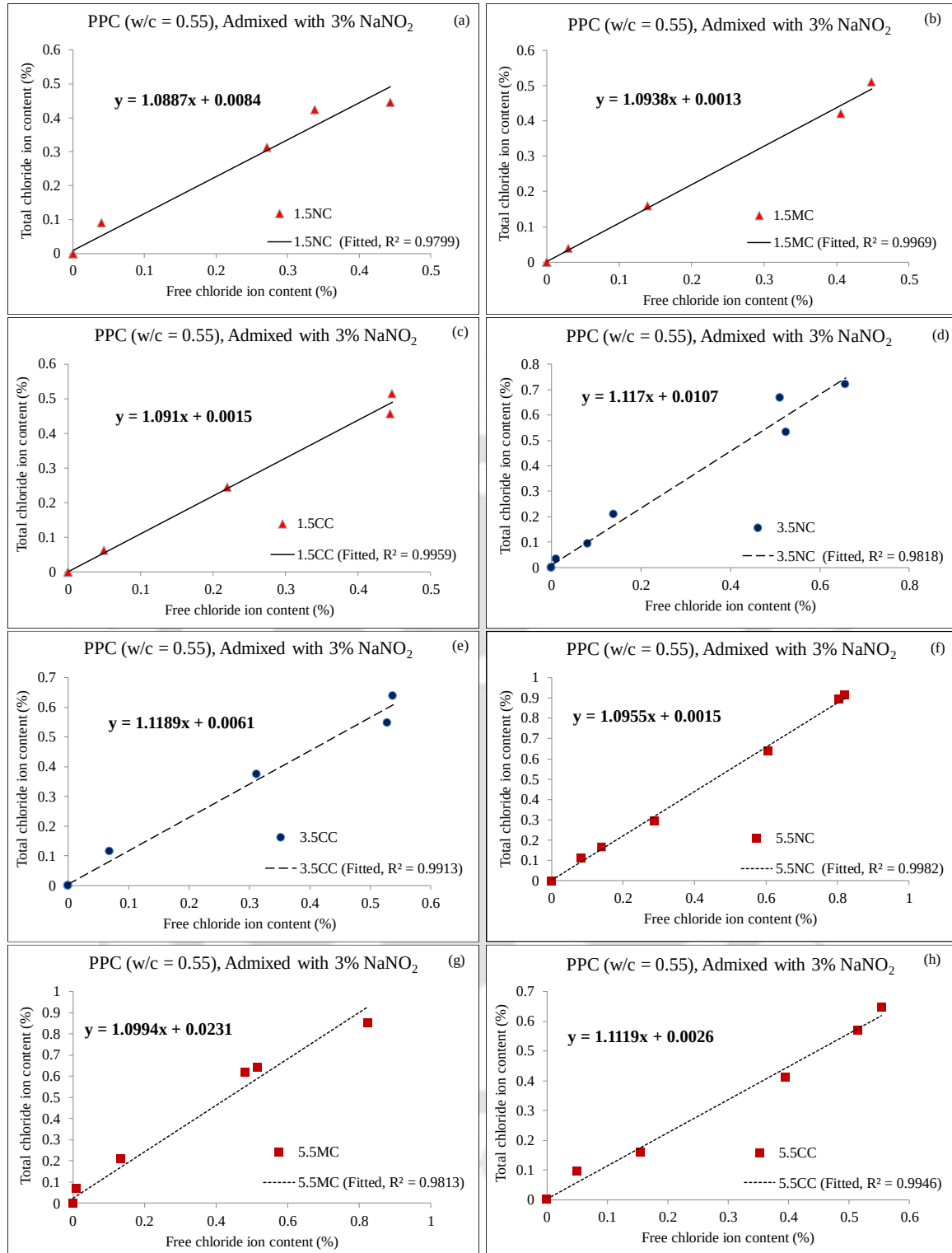
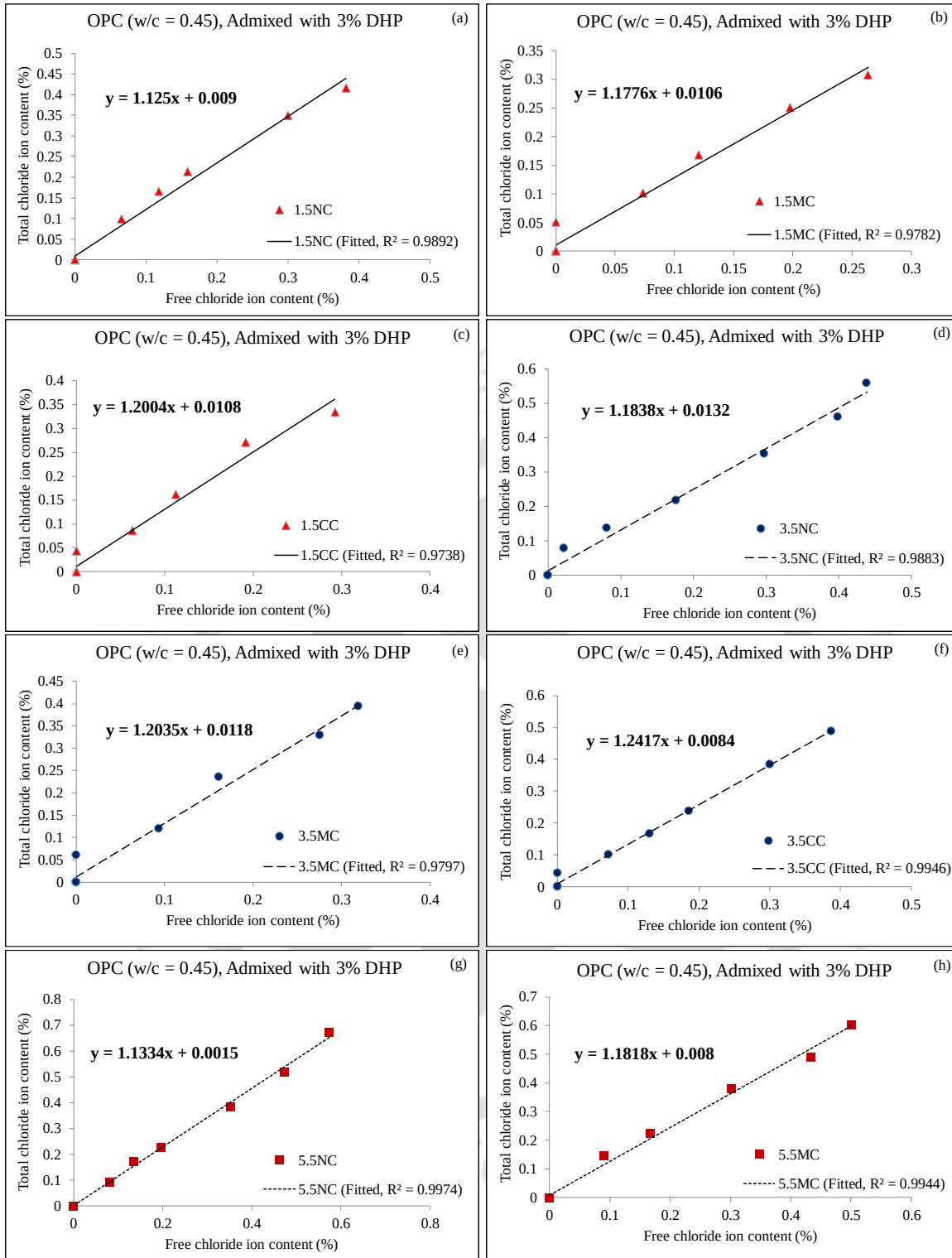


Fig. B14 Relationship between free chloride ion and total chloride ion contents of PPC concrete containing 3% NaNO₂ at w/c of 0.55 and exposed to chloride salt solutions of different concentrations: (a) 1.5% NaCl, (b) 1.5% MgCl₂, (c) 1.5% CaCl₂, (d) 3.5% NaCl, (e) 3.5% CaCl₂, (f) 5.5% NaCl, (g) 5.5% MgCl₂, and (h) 5.5% CaCl₂



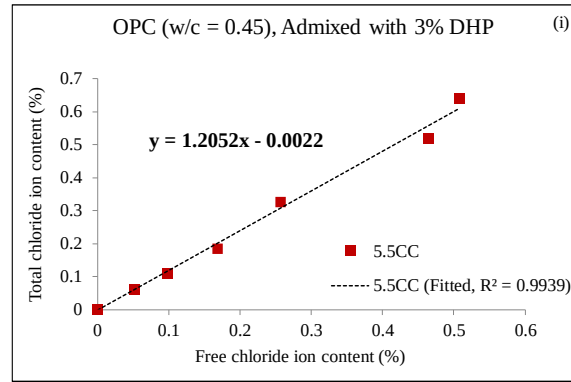
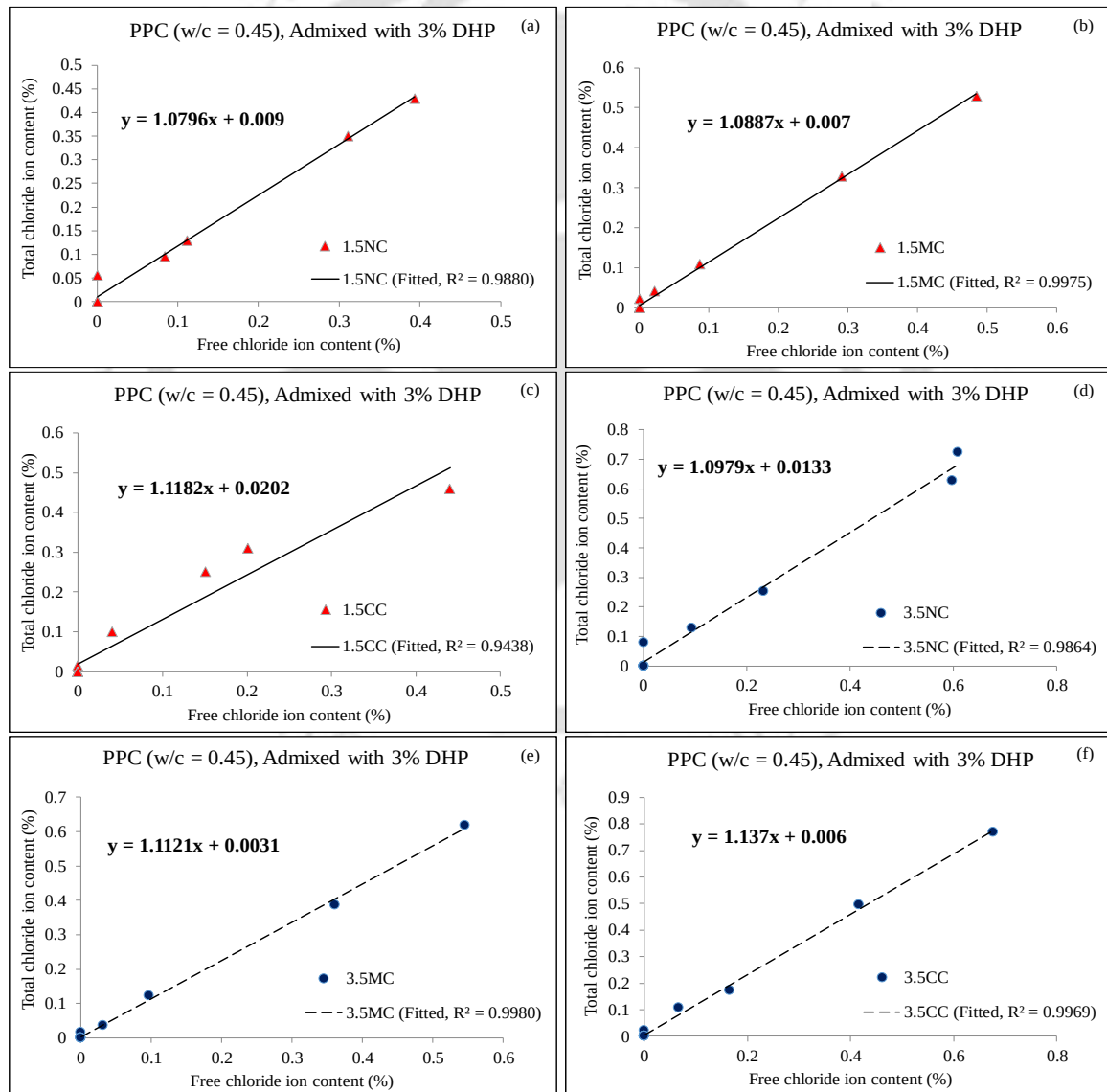


Fig. B15 Relationship between free chloride ion and total chloride ion contents of OPC concrete containing 3% DHP at w/c of 0.45 and exposed to chloride salt solutions of different concentrations: (a) 1.5% NaCl, (b) 1.5% MgCl₂, (c) 1.5% CaCl₂, (d) 3.5% NaCl, (e) 3.5% MgCl₂, (f) 3.5% CaCl₂, (g) 5.5% NaCl, (h) 5.5% MgCl₂, and (i) 5.5% CaCl₂



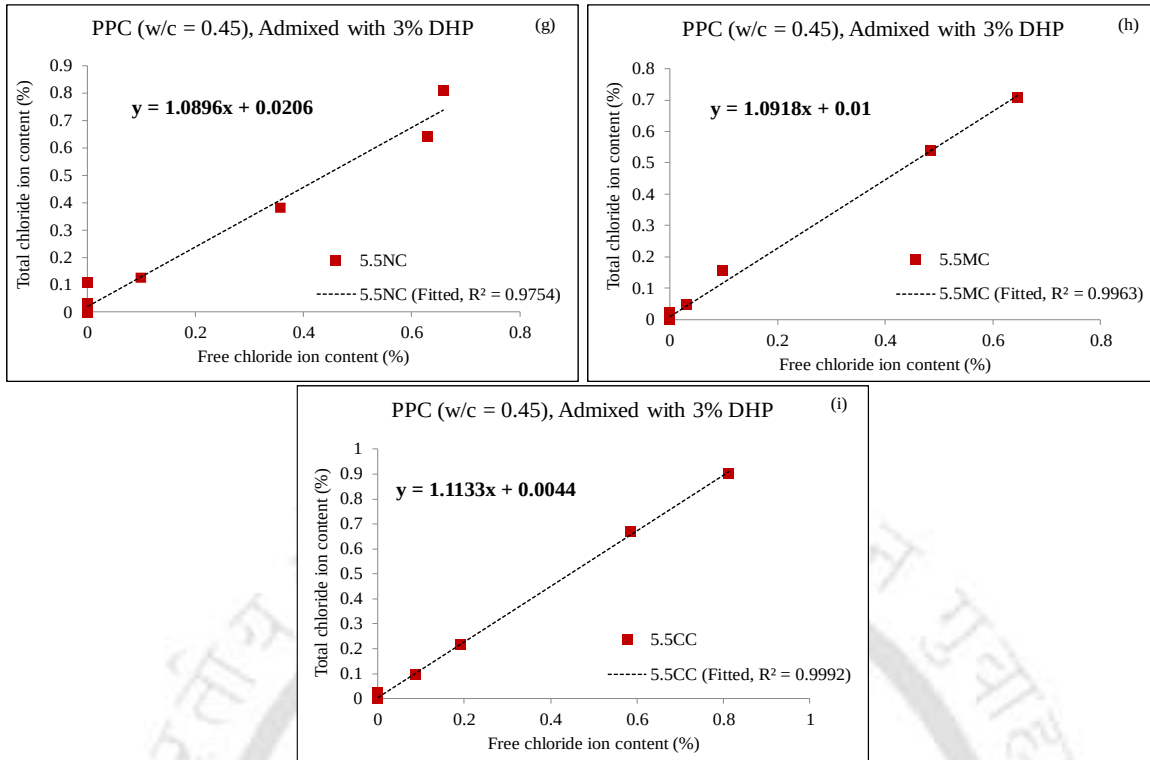
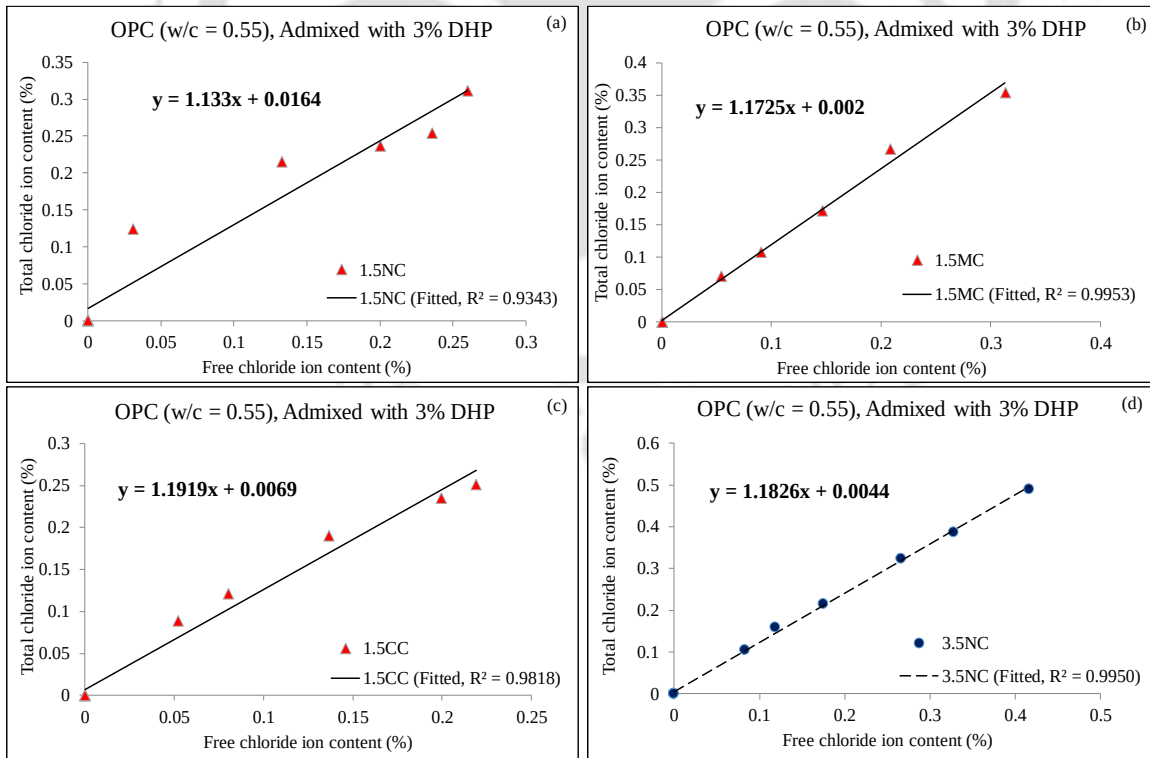


Fig. B16 Relationship between free chloride ion and total chloride ion contents of PPC concrete containing 3% DHP at w/c of 0.45 and exposed to chloride salt solutions of different concentrations: (a) 1.5% NaCl, (b) 1.5% MgCl₂, (c) 1.5% CaCl₂, (d) 3.5% NaCl, (e) 3.5% MgCl₂, (f) 3.5% CaCl₂, (g) 5.5% NaCl, (h) 5.5% MgCl₂, and (i) 5.5% CaCl₂



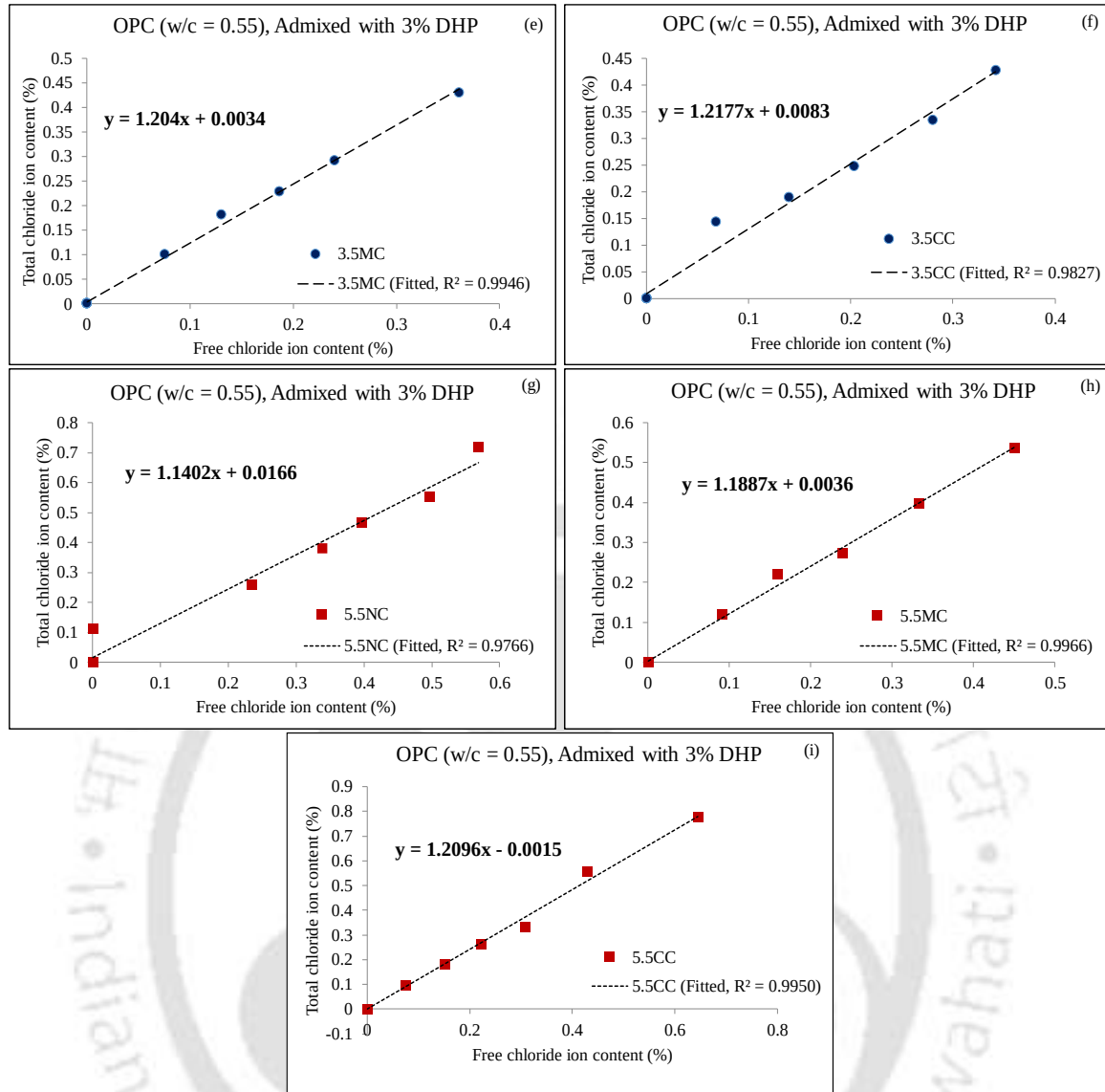
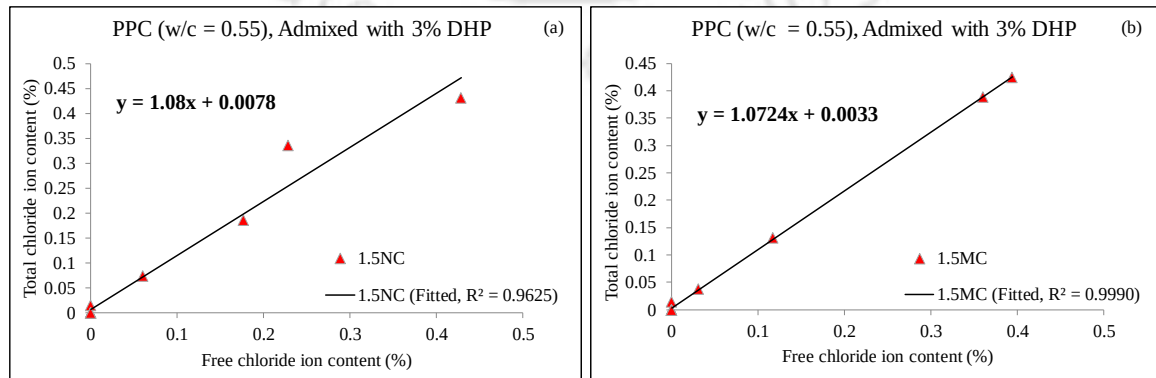


Fig. B17 Relationship between free chloride ion and total chloride ion contents of OPC concrete containing 3% DHP at w/c of 0.55 and exposed to chloride salt solutions of different concentrations: (a) 1.5% NaCl, (b) 1.5% MgCl₂, (c) 1.5% CaCl₂, (d) 3.5% NaCl, (e) 3.5% MgCl₂, (f) 3.5% CaCl₂, (g) 5.5% NaCl, (h) 5.5% MgCl₂, and (i) 5.5% CaCl₂



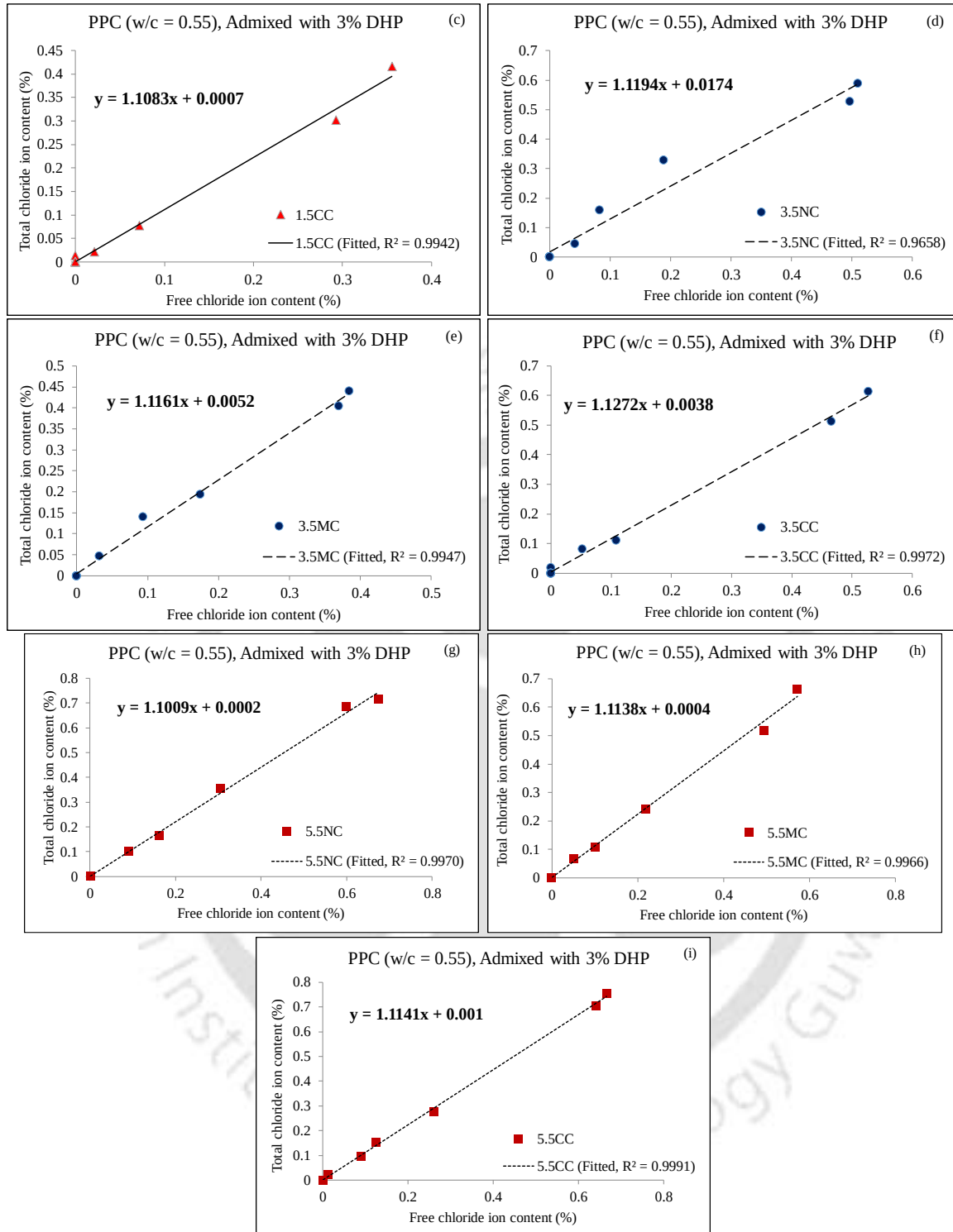


Fig. B18 Relationship between free chloride ion and total chloride ion contents of PPC concrete containing 3% DHP at w/c of 0.55 and exposed to chloride salt solutions of different concentrations: (a) 1.5% NaCl, (b) 1.5% MgCl₂, (c) 1.5% CaCl₂, (d) 3.5% NaCl, (e) 3.5% MgCl₂, (f) 3.5% CaCl₂, (g) 5.5% NaCl, (h) 5.5% MgCl₂, and (i) 5.5% CaCl₂

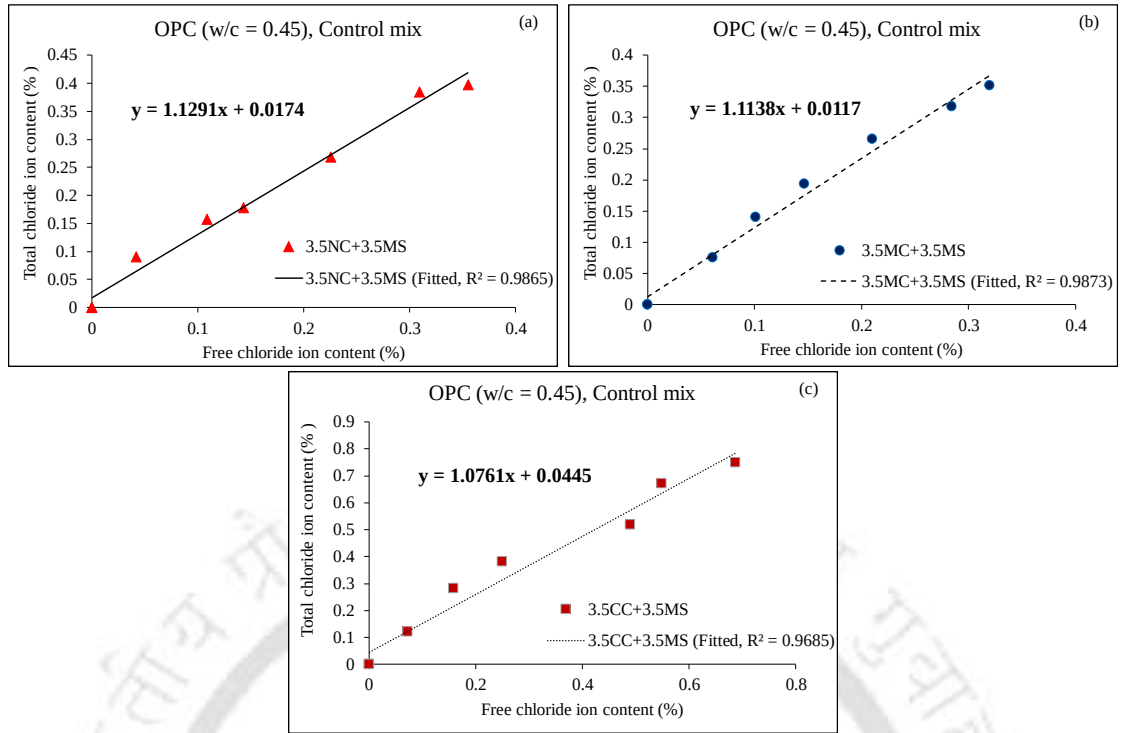


Fig. B19 Relationship between free chloride ion and total chloride ion contents of OPC control concrete (without corrosion inhibitors) at w/c of 0.45 and exposed to composite chloride-sulfate solutions: (a) 3.5% NaCl+3.5% MgSO₄, (b) 3.5% MgCl₂+3.5% MgSO₄, and (c) 3.5% CaCl₂+3.5% MgSO₄

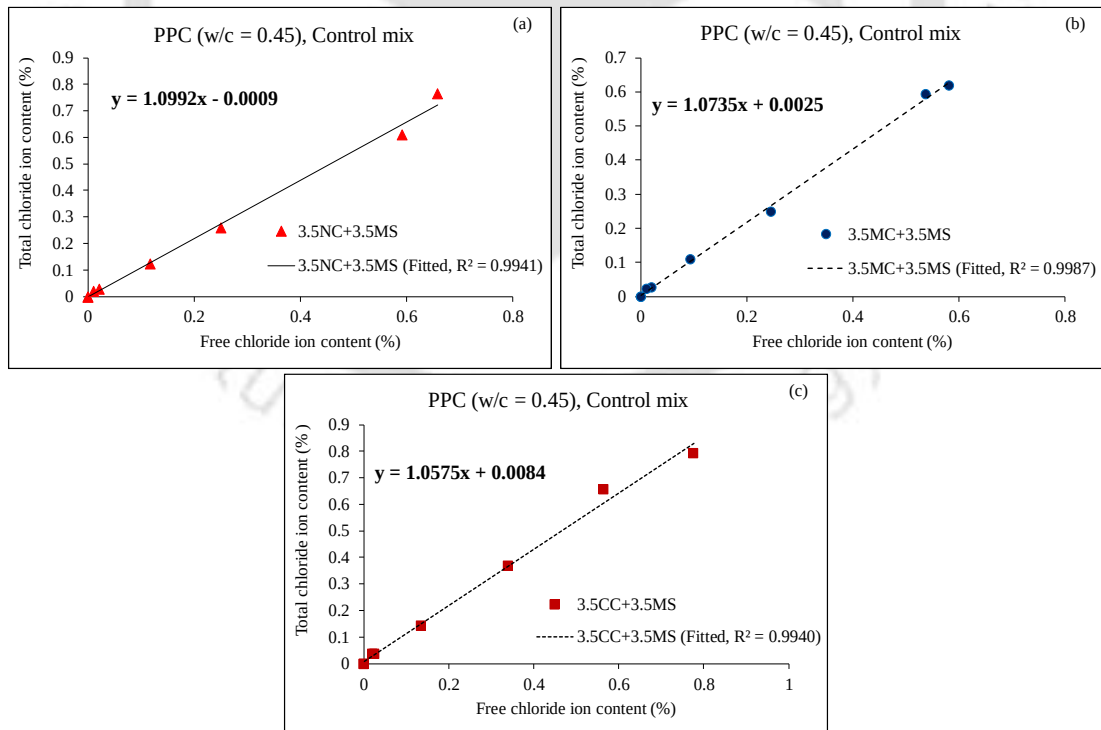


Fig. B20 Relationship between free chloride ion and total chloride ion contents of PPC control concrete (without corrosion inhibitors) at w/c of 0.45 and exposed to composite chloride-sulfate solutions: (a) 3.5% NaCl+3.5% MgSO₄, (b) 3.5% MgCl₂+3.5% MgSO₄, and (c) 3.5% CaCl₂+3.5% MgSO₄

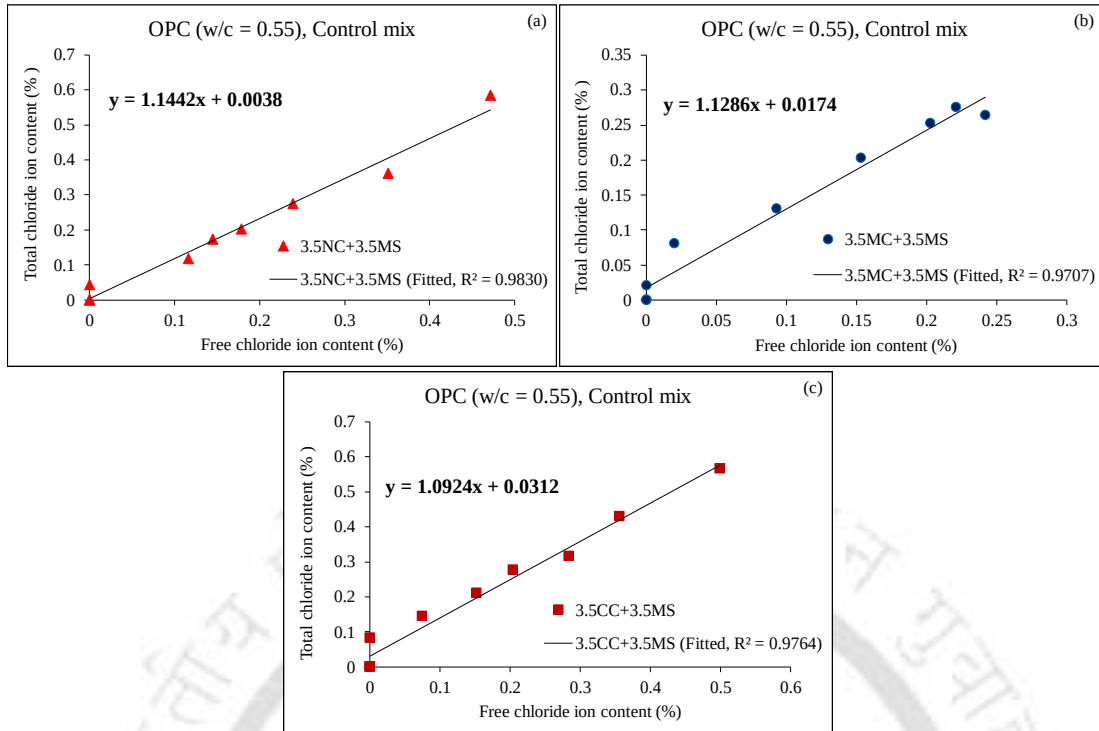


Fig. B21 Relationship between free chloride ion and total chloride ion contents of OPC control concrete (without corrosion inhibitors) at w/c of 0.55 and exposed to composite chloride-sulfate solutions: (a) 3.5% NaCl+3.5% MgSO₄, (b) 3.5% MgCl₂+3.5% MgSO₄, and (c) 3.5% CaCl₂+3.5% MgSO₄

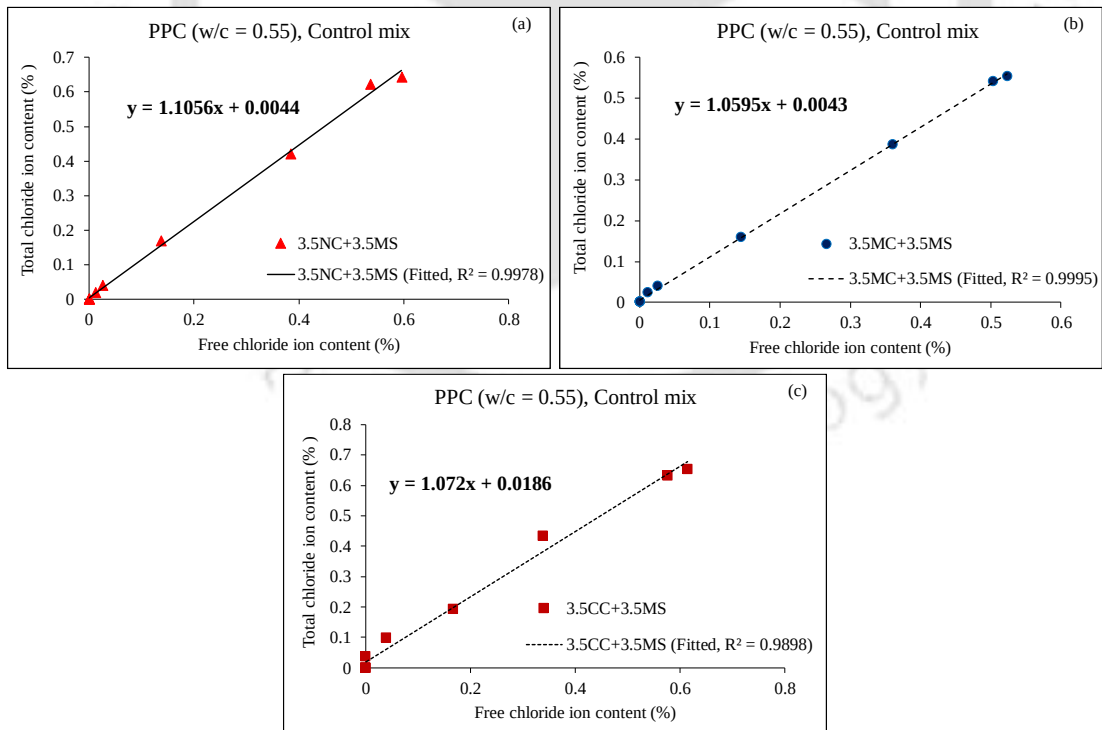


Fig. B22 Relationship between free chloride ion and total chloride ion contents of PPC control concrete (without corrosion inhibitors) at w/c of 0.55 and exposed to composite chloride-sulfate solutions: (a) 3.5% NaCl+3.5% MgSO₄, (b) 3.5% MgCl₂+3.5% MgSO₄, and (c) 3.5% CaCl₂+3.5% MgSO₄

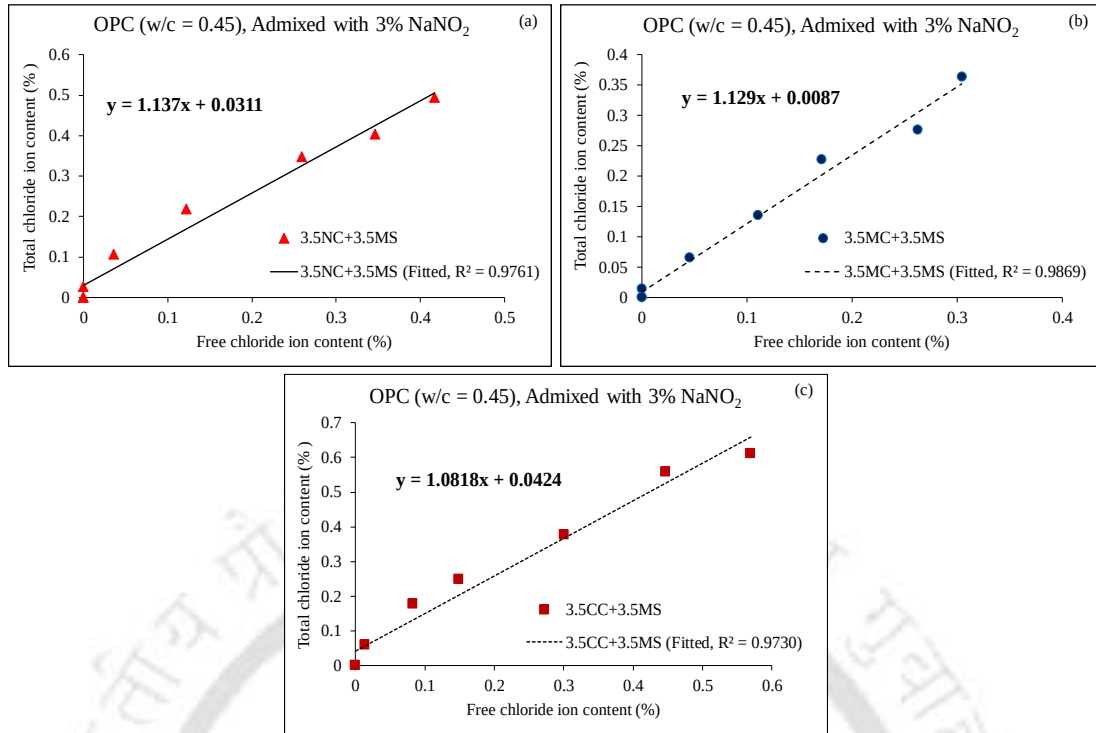


Fig. B23 Relationship between free chloride ion and total chloride ion contents of OPC concrete containing 3% NaNO₂ at w/c of 0.45 and exposed to composite chloride-sulfate solutions: (a) 3.5% NaCl+3.5% MgSO₄, (b) 3.5% MgCl₂+3.5% MgSO₄, and (c) 3.5% CaCl₂+3.5% MgSO₄

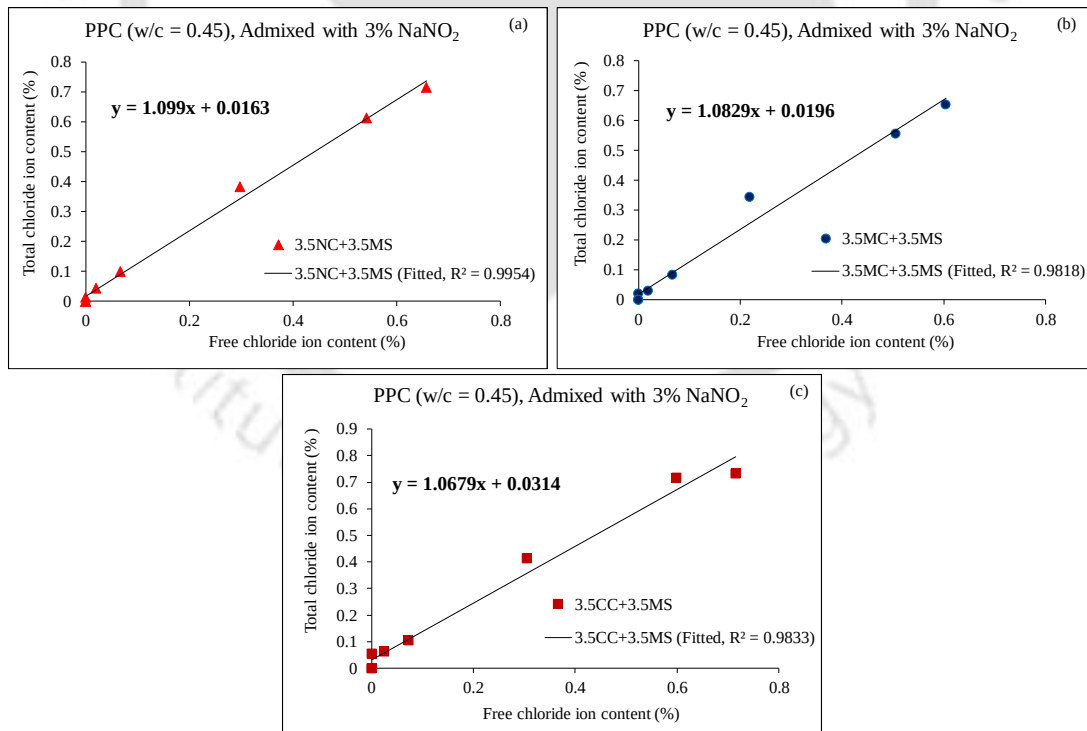


Fig. B24 Relationship between free chloride ion and total chloride ion contents of PPC concrete containing 3% NaNO₂ at w/c of 0.45 and exposed to composite chloride-sulfate solutions: (a) 3.5% NaCl+3.5% MgSO₄, (b) 3.5% MgCl₂+3.5% MgSO₄, and (c) 3.5% CaCl₂+3.5% MgSO₄

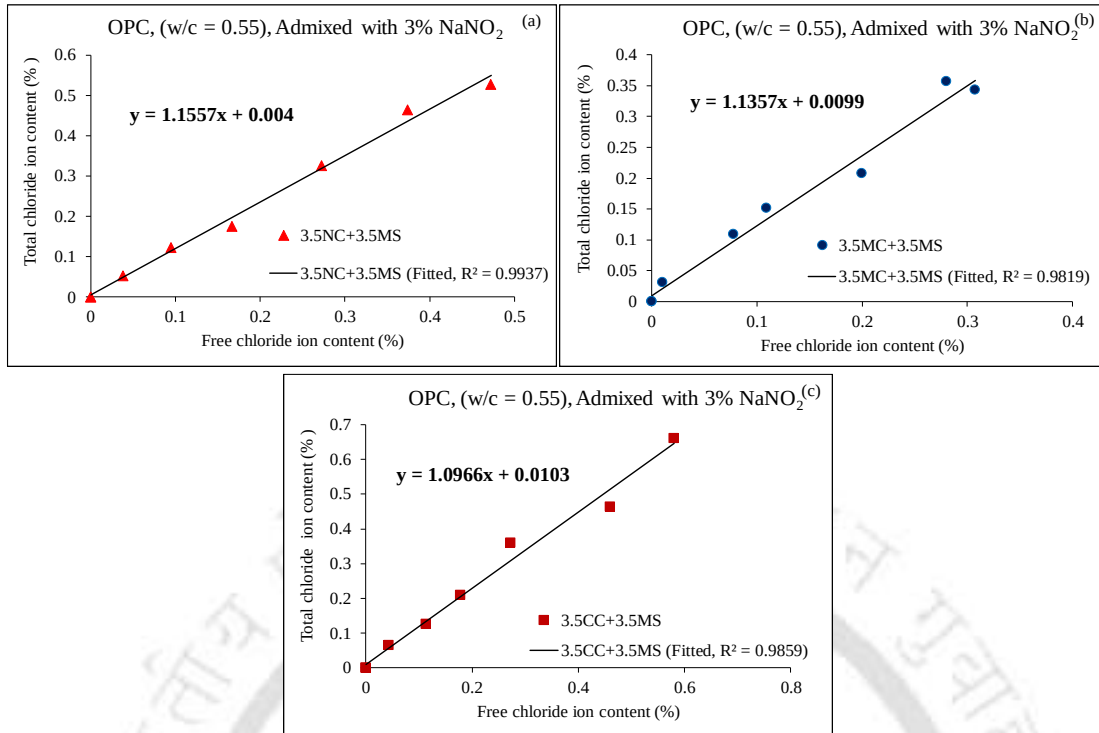


Fig. B25 Relationship between free chloride ion and total chloride ion contents of OPC concrete containing 3% NaNO₂ at w/c of 0.55 and exposed to composite chloride-sulfate solutions: (a) 3.5% NaCl+3.5% MgSO₄, (b) 3.5% MgCl₂+3.5% MgSO₄, and (c) 3.5% CaCl₂+3.5% MgSO₄

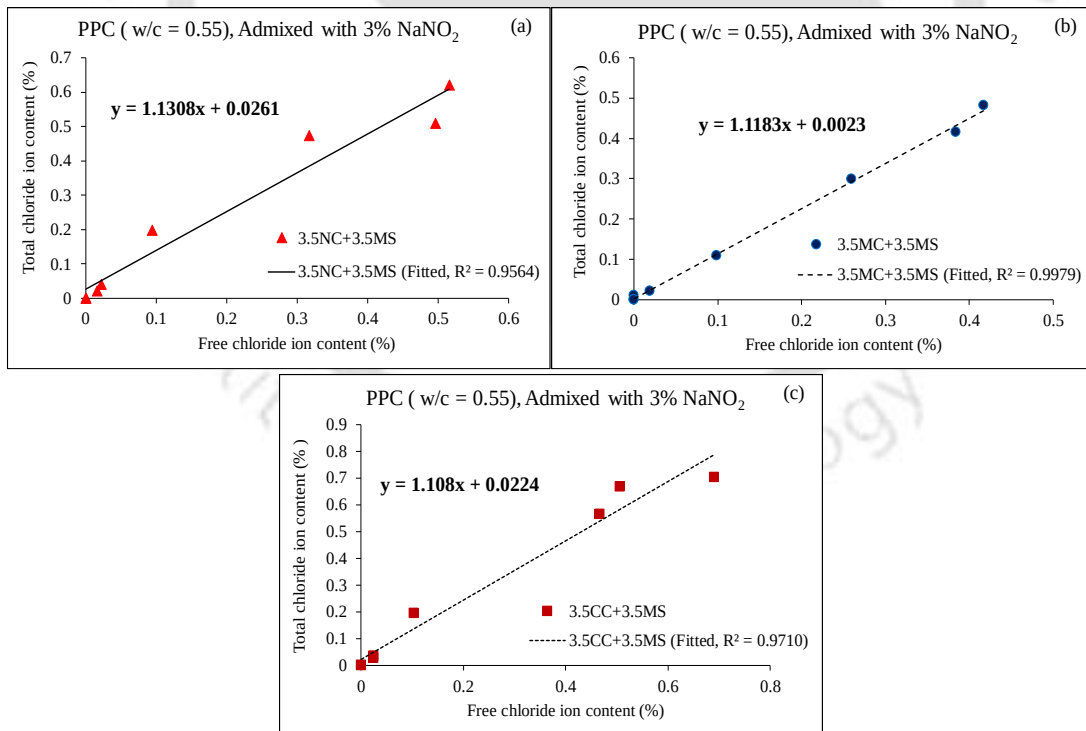


Fig. B26 Relationship between free chloride ion and total chloride ion contents of PPC concrete containing 3% NaNO₂ at w/c of 0.55 and exposed to composite chloride-sulfate solutions: (a) 3.5% NaCl+3.5% MgSO₄, (b) 3.5% MgCl₂+3.5% MgSO₄, and (c) 3.5% CaCl₂+3.5% MgSO₄

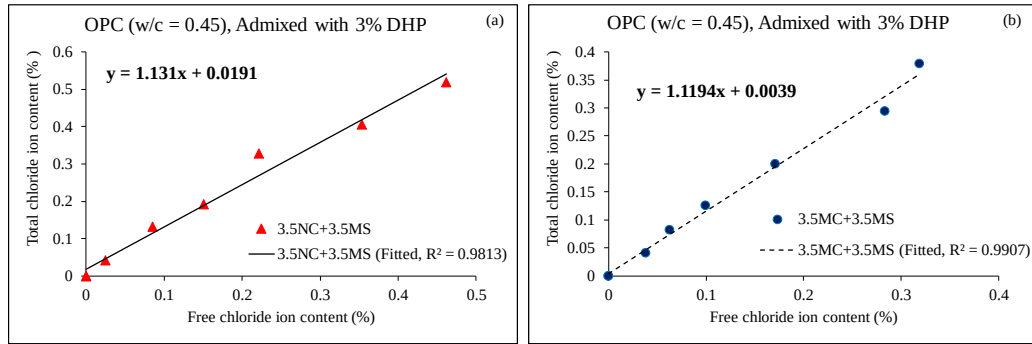


Fig. B27 Relationship between free chloride ion and total chloride ion contents of OPC concrete containing 3% DHP at w/c of 0.45 and exposed to composite chloride-sulfate solutions: (a) 3.5% NaCl+3.5% MgSO₄, and (b) 3.5% MgCl₂+3.5% MgSO₄

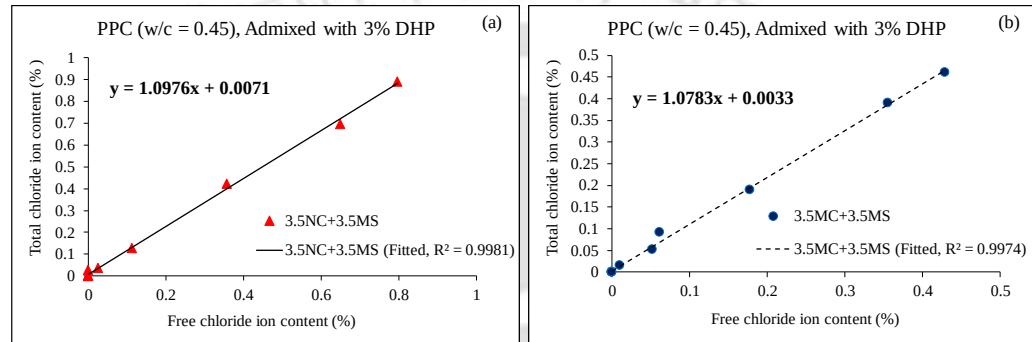


Fig. B28 Relationship between free chloride ion and total chloride ion contents of PPC concrete containing 3% DHP at w/c of 0.45 and exposed to composite chloride-sulfate solutions: (a) 3.5% NaCl+3.5% MgSO₄, and (b) 3.5% MgCl₂+3.5% MgSO₄

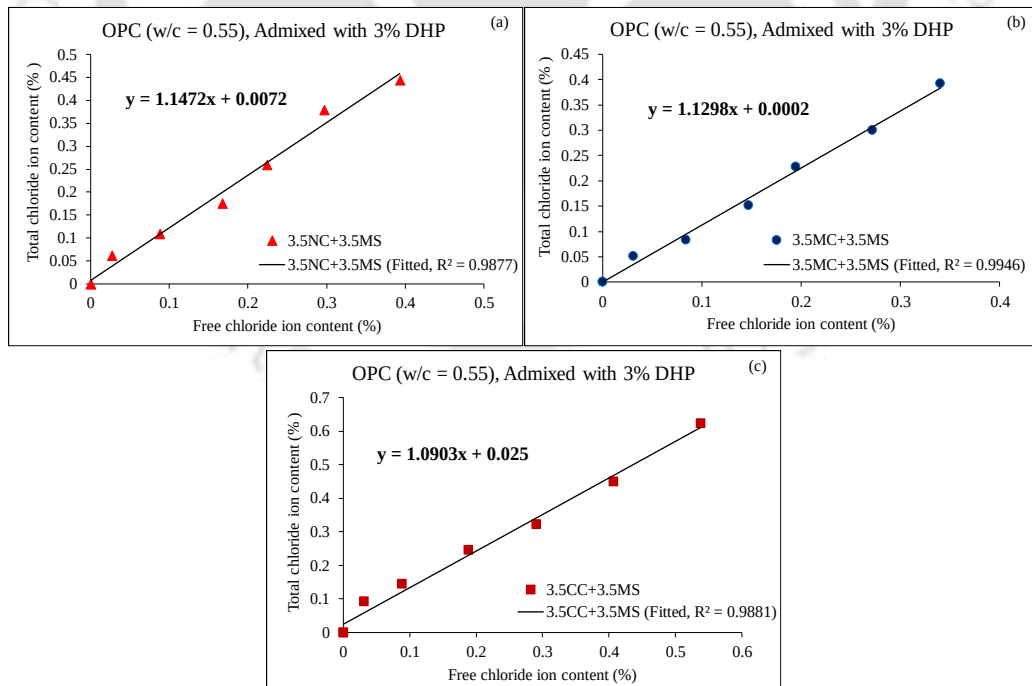


Fig. B29 Relationship between free chloride ion and total chloride ion contents of OPC concrete containing 3% DHP at w/c of 0.55 and exposed to composite chloride-sulfate solutions: (a) 3.5% NaCl+3.5% MgSO₄, (b) 3.5% MgCl₂+3.5% MgSO₄, and (c) 3.5% CaCl₂+3.5% MgSO₄

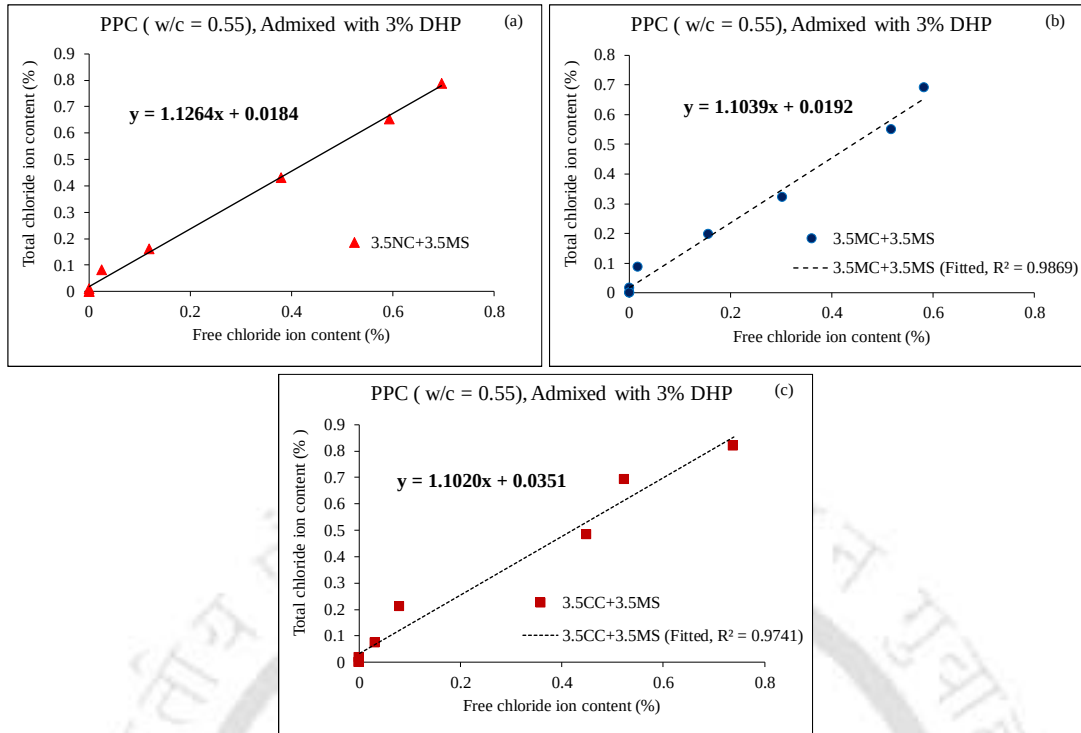


Fig. B30 Relationship between free chloride ion and total chloride ion contents of PPC concrete containing 3% DHP at w/c of 0.55 and exposed to composite chloride-sulfate solutions: (a) 3.5% NaCl+3.5% MgSO₄, (b) 3.5% MgCl₂+3.5% MgSO₄, and (c) 3.5% CaCl₂+3.5% MgSO₄

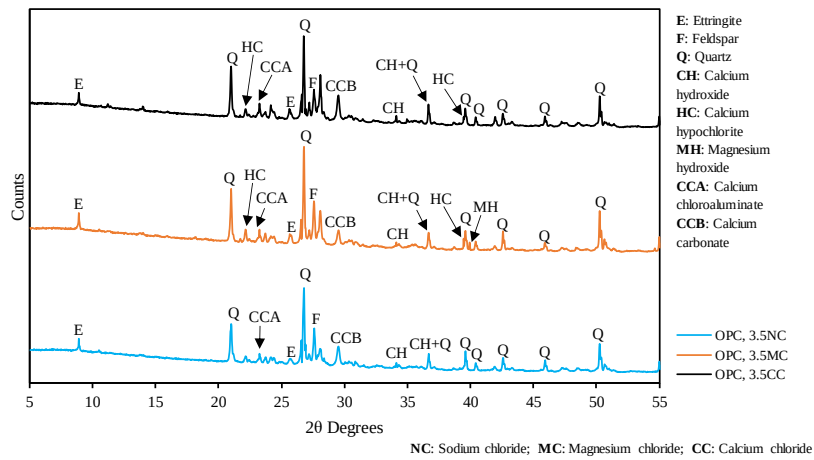


Fig. B31 XRD patterns of control concrete made from OPC at w/c of 0.55, and exposed to different chloride salt solutions

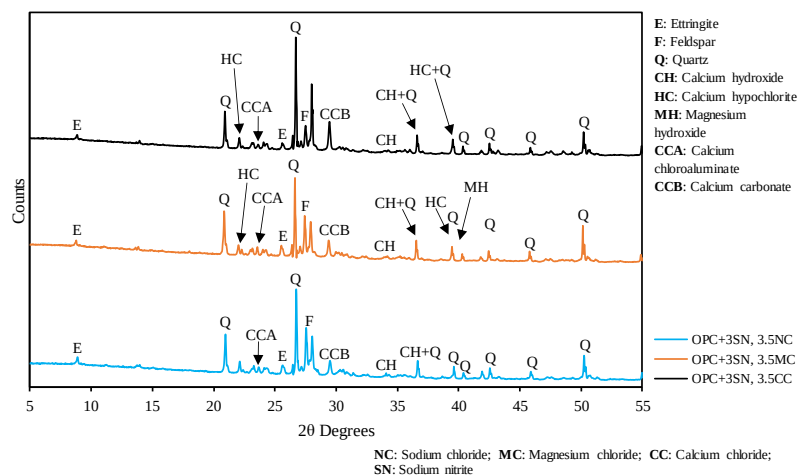


Fig. B32 XRD patterns of OPC concrete containing 3% NaNO_2 at w/c of 0.45, and exposed to different chloride salt solutions

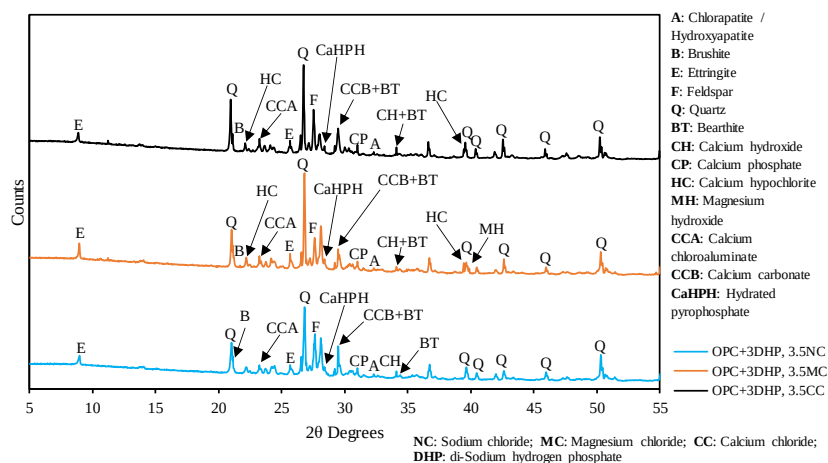


Fig. B33 XRD patterns of OPC concrete containing 3% DHP at w/c of 0.55, and exposed to different chloride salt solutions

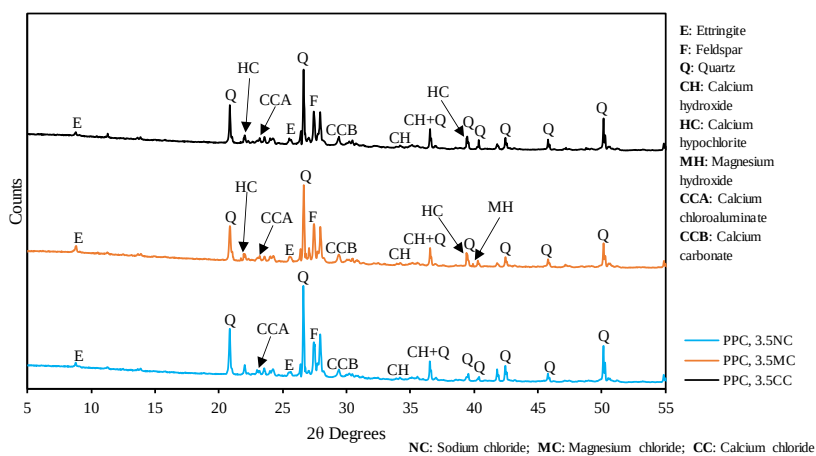


Fig. B34 XRD patterns of control concrete made from PPC at w/c of 0.55, and exposed to different chloride salt solutions

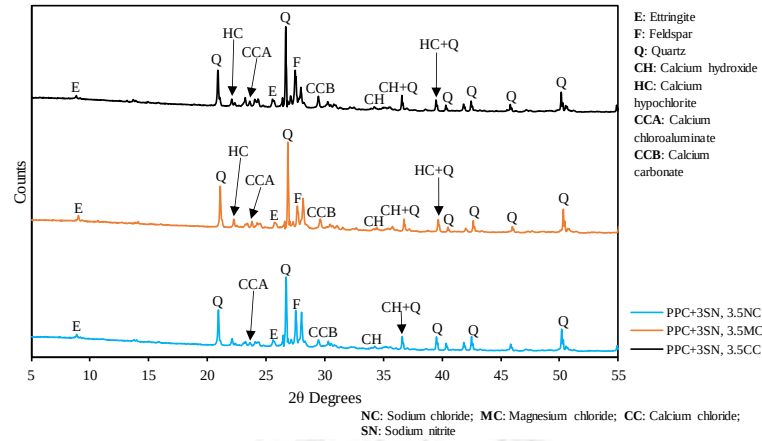


Fig. B35 XRD patterns of PPC concrete containing 3% NaNO_2 at w/c of 0.45, and exposed to different chloride salt solutions

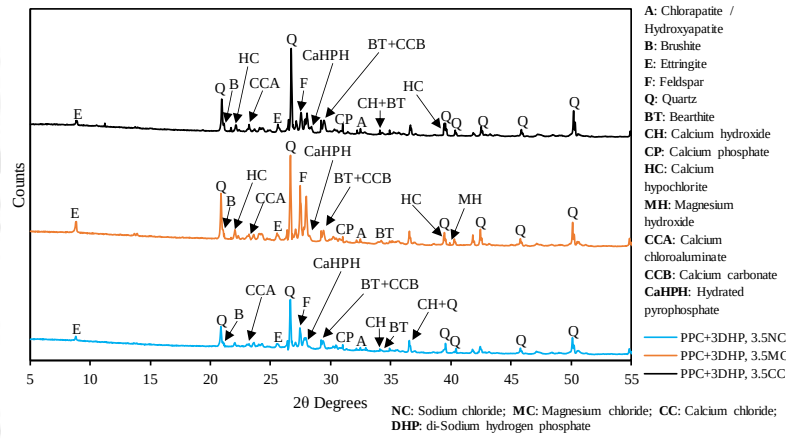


Fig. B36 XRD patterns of PPC concrete containing 3% DHP at w/c of 0.55, and exposed to different chloride salt solutions

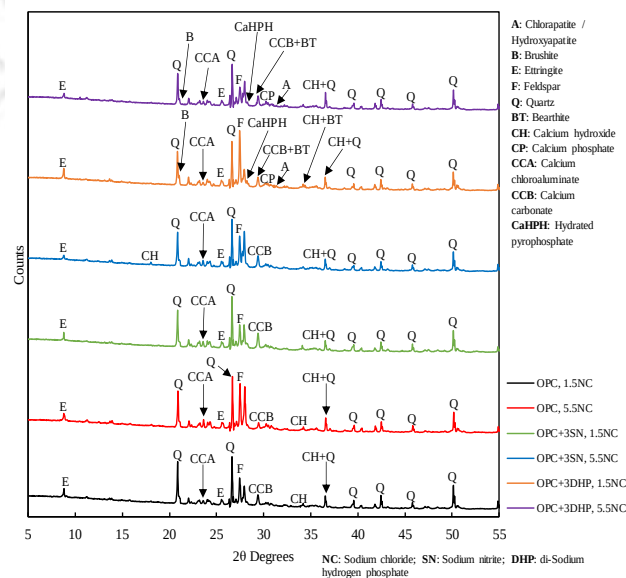


Fig. B37 XRD patterns of control OPC concrete and that admixed with corrosion inhibitors at w/c of 0.55, and exposed to NaCl solutions of different concentrations (1.5% and 5.5%)

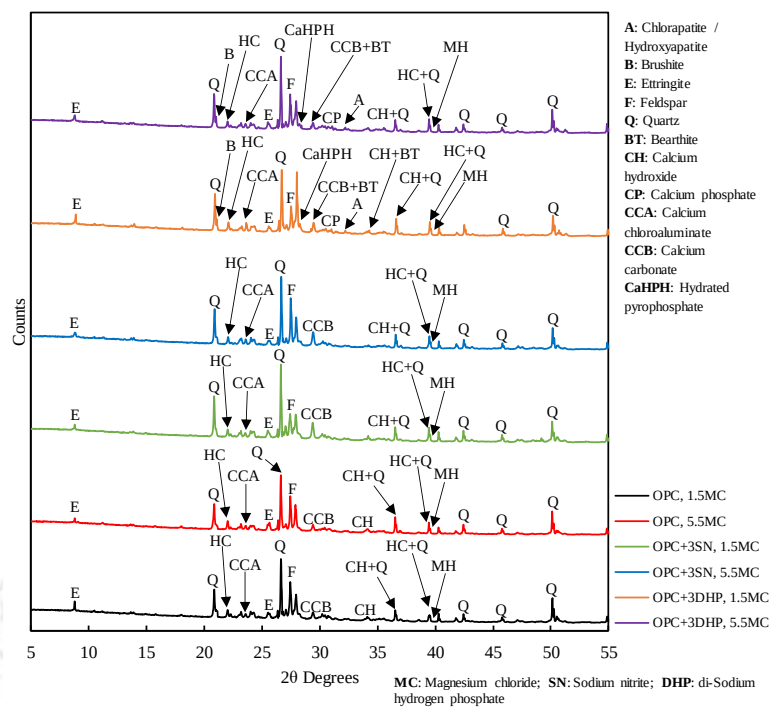


Fig. B38 XRD patterns of control OPC concrete and that admixed with corrosion inhibitors at w/c of 0.55, and exposed to $MgCl_2$ solutions of different concentrations (1.5% and 5.5%)

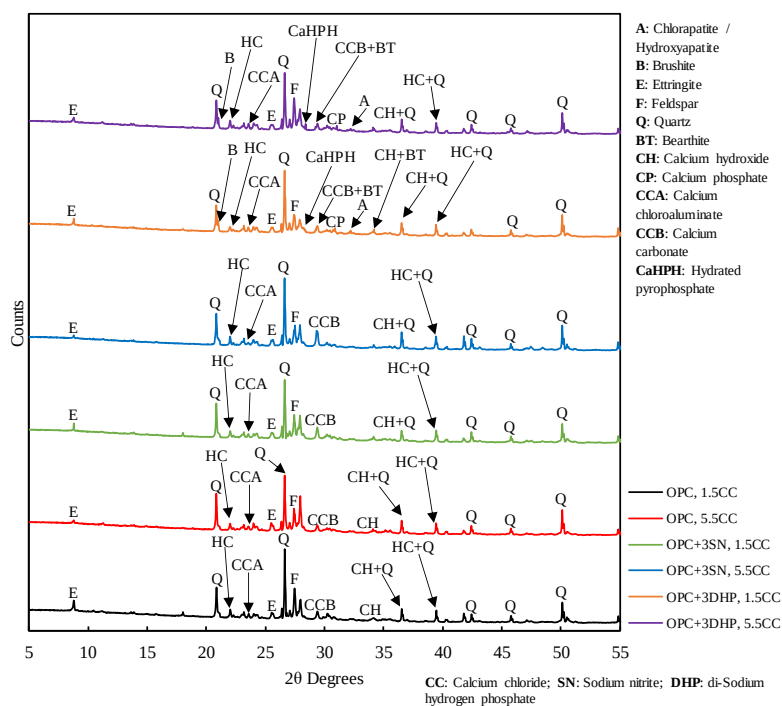


Fig. B39 XRD patterns of control OPC concrete and that admixed with corrosion inhibitors at w/c of 0.55, and exposed to $CaCl_2$ solutions of different concentrations (1.5% and 5.5%)

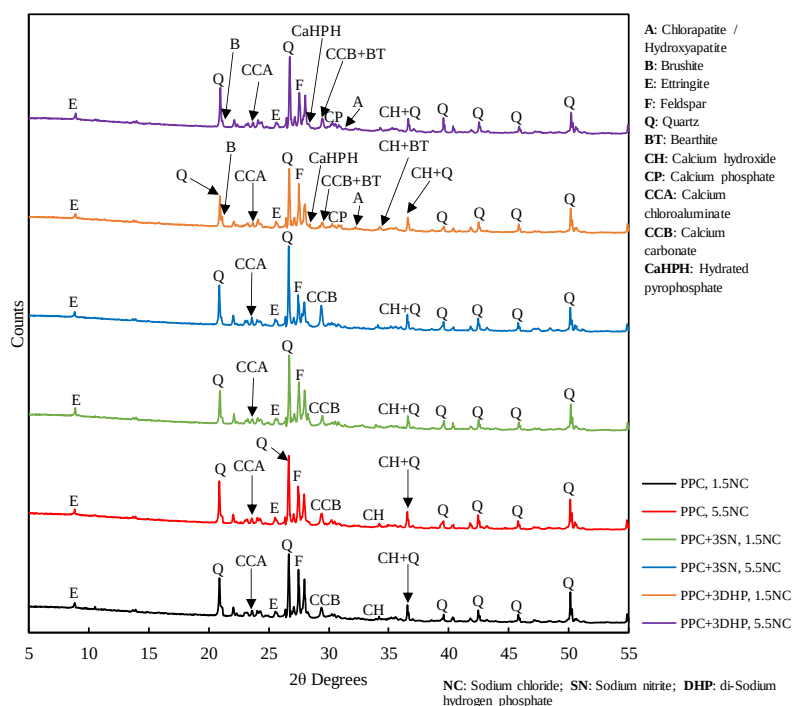


Fig. B40 XRD patterns of control PPC concrete and that admixed with corrosion inhibitors at w/c of 0.55, and exposed to NaCl solutions of different concentrations (1.5% and 5.5%)

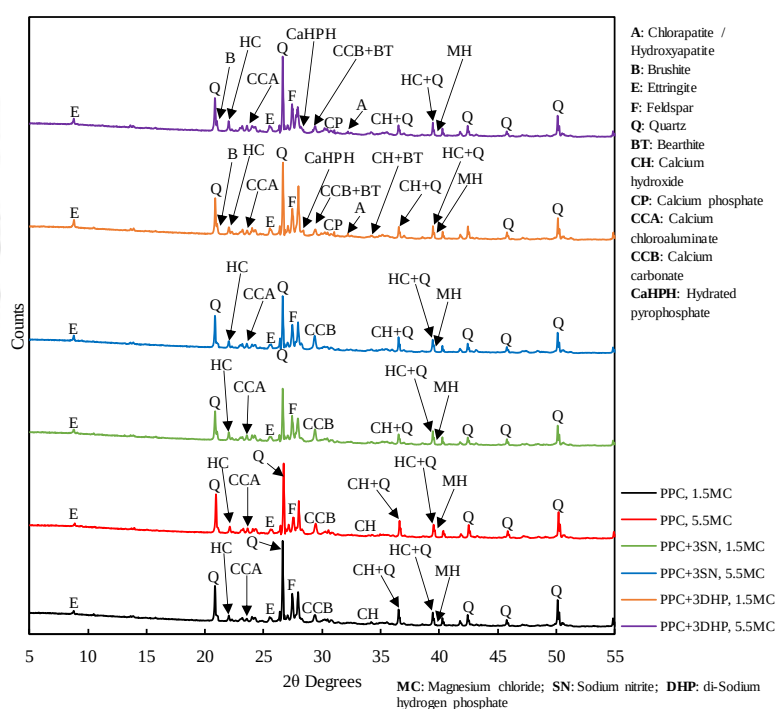


Fig. B41 XRD patterns of control PPC concrete and that admixed with corrosion inhibitors at w/c of 0.55, and exposed to $MgCl_2$ solutions of different concentrations (1.5% and 5.5%)

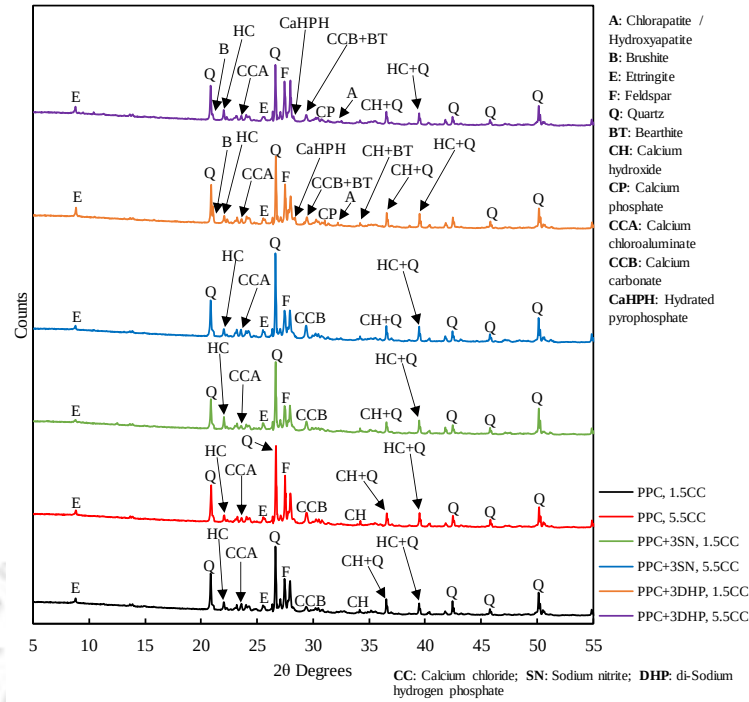


Fig. B42 XRD patterns of control PPC concrete and that admixed with corrosion inhibitors at w/c of 0.55, and exposed to CaCl_2 solutions of different concentrations (1.5% and 5.5%)

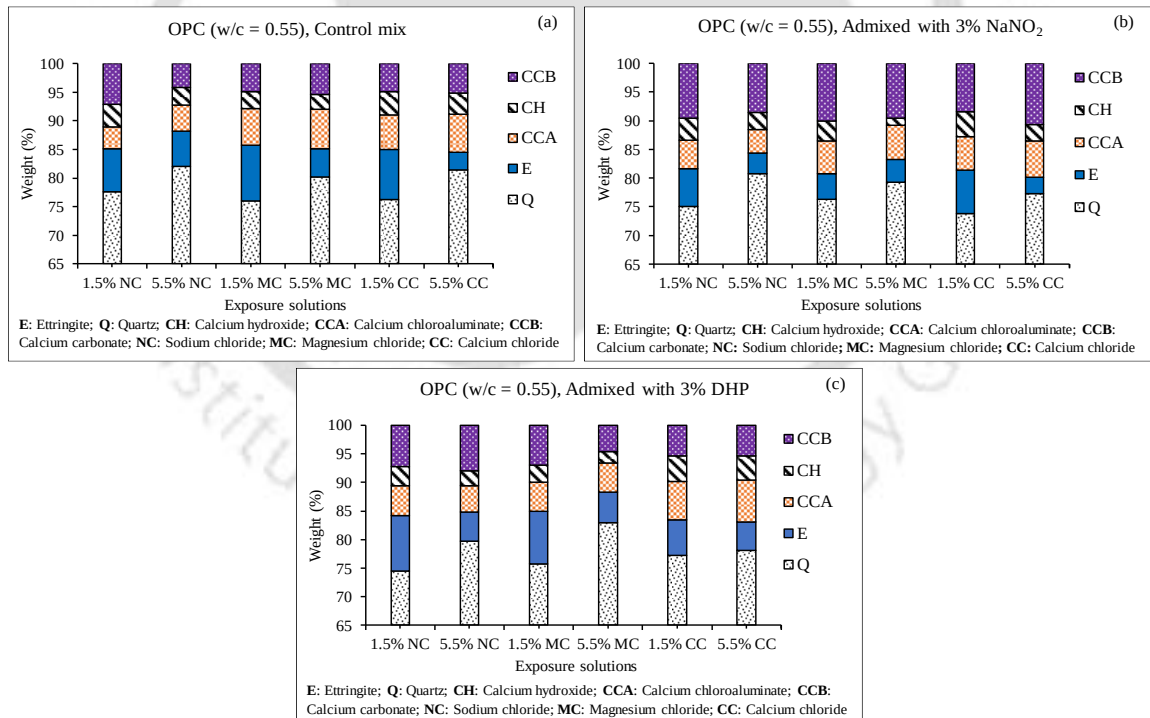


Fig. B43 Weight (%) of compounds from XRD patterns of OPC concrete at w/c of 0.55, and exposed to chloride solutions of different concentrations (1.5%, and 5.5%): (a) control mix, (b) concrete admixed with 3% NaNO_2 , and (c) concrete admixed with 3% DHP

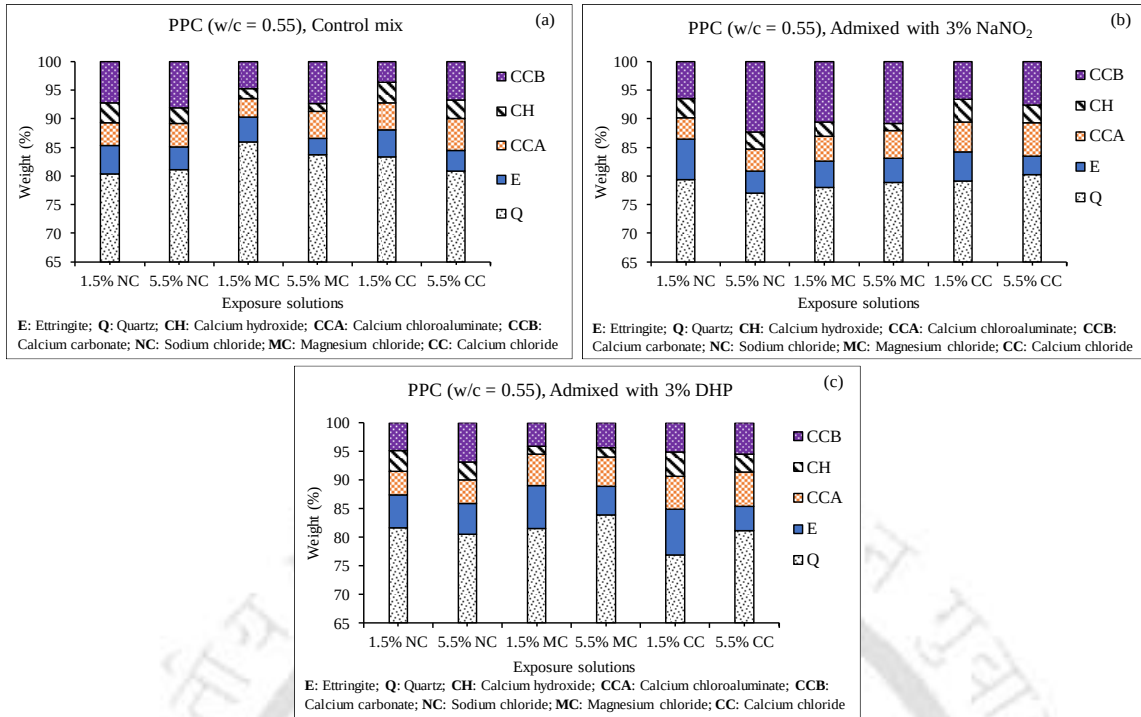


Fig. B44 Weight (%) of compounds from XRD patterns of PPC concrete at w/c of 0.55, and exposed to chloride solutions of different concentrations (1.5%, and 5.5%): (a) control mix, (b) concrete admixed with 3% NaNO₂, and (c) concrete admixed with 3% DHP

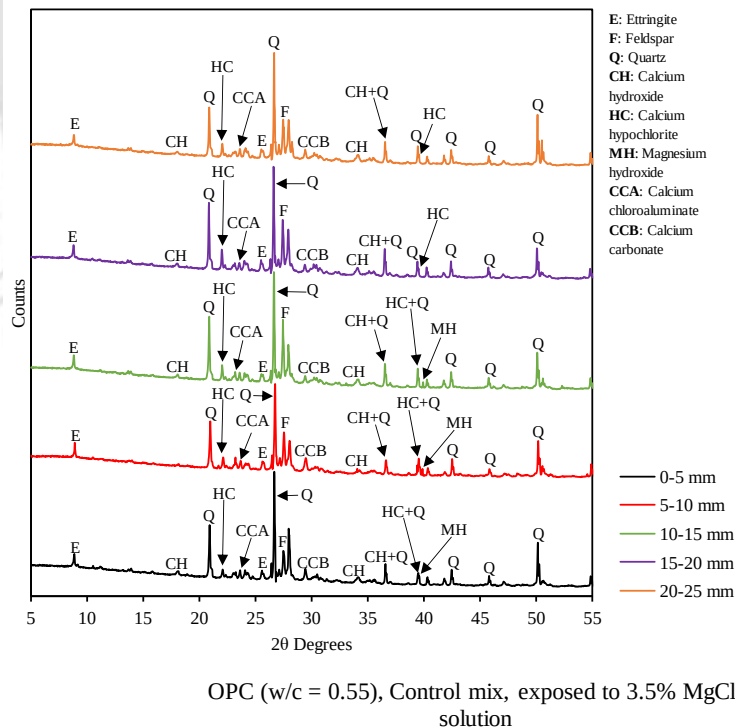


Fig. B45 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, 15-20 mm, and 20-25 mm from the exposure surface of control concrete made from OPC at w/c of 0.55, and exposed to 3.5% MgCl₂ solution

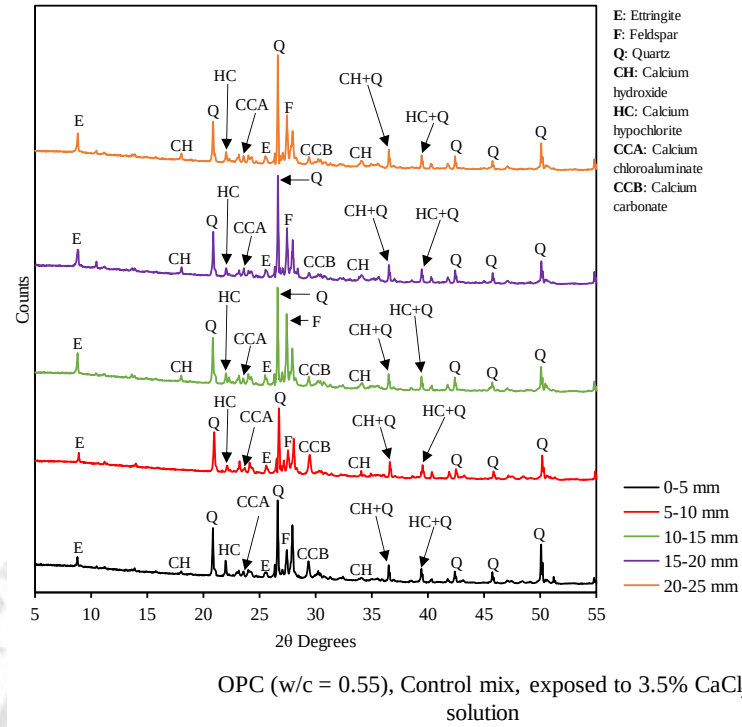


Fig. B46 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, 15-20 mm and 20-25 mm from the exposure surface of control concrete made from OPC at w/c of 0.55, and exposed to 3.5% CaCl_2 solution

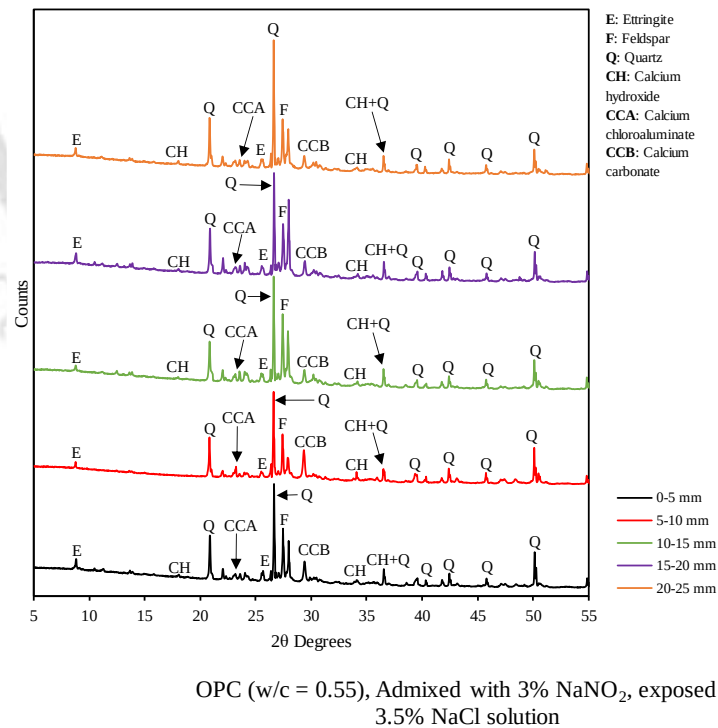


Fig. B47 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, 15-20 mm and 20-25 mm from the exposure surface of OPC concrete admixed with 3% NaNO_2 at w/c of 0.55, and exposed to 3.5% NaCl solution

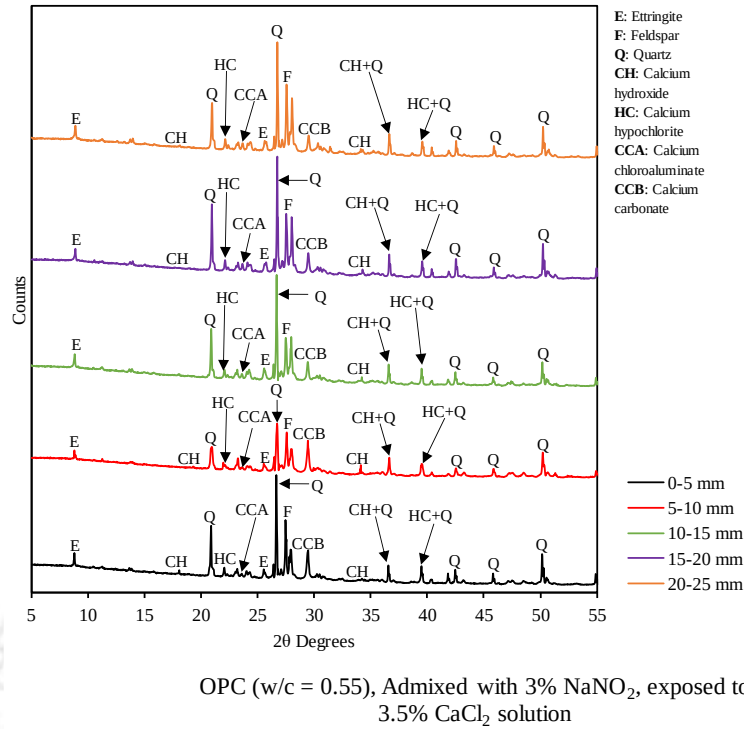


Fig. B48 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, 15-20 mm and 20-25 mm from the exposure surface of OPC concrete admixed with 3% NaNO₂ at w/c of 0.55, and exposed to 3.5% CaCl₂ solution

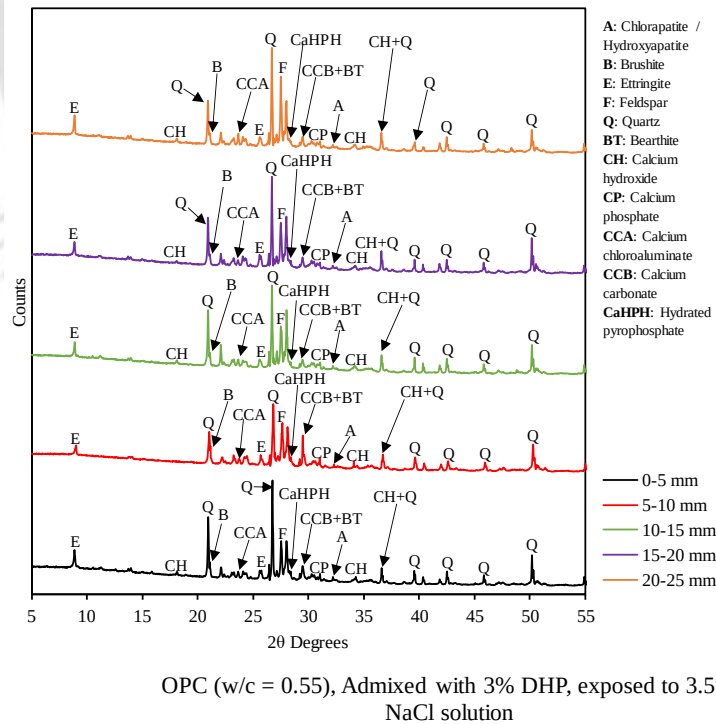


Fig. B49 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, 15-20 mm and 20-25 mm from the exposure surface of OPC concrete admixed with 3% DHP at w/c of 0.55, and exposed to 3.5% NaCl solution

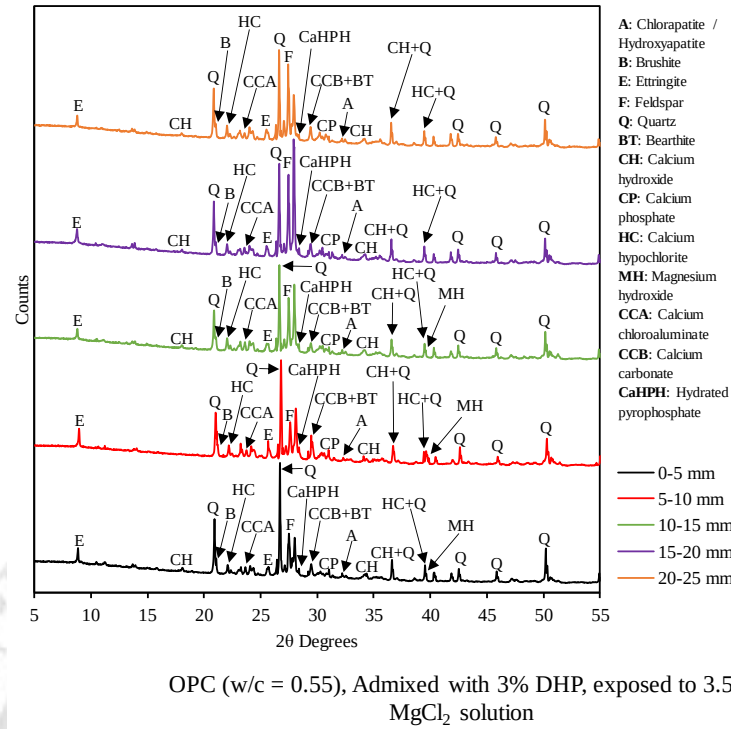


Fig. B50 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, 15-20 mm and 20-25 mm from the exposure surface of OPC concrete admixed with 3% DHP at w/c of 0.55, and exposed to 3.5% $MgCl_2$ solution

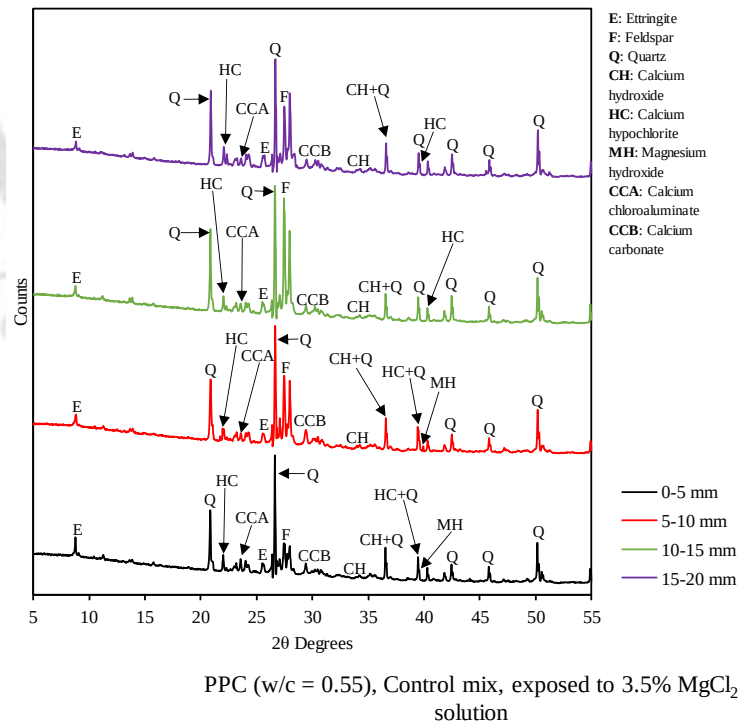


Fig. B51 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, and 15-20 mm from the exposure surface of control concrete made from PPC at w/c of 0.55, and exposed to 3.5% $MgCl_2$ solution

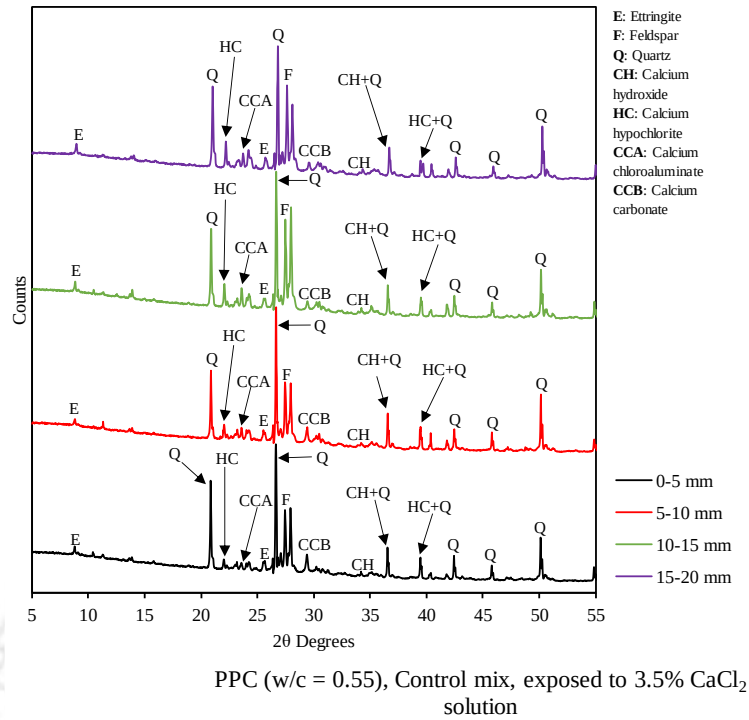


Fig. B52 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, and 15-20 mm from the exposure surface of control concrete made from PPC at w/c of 0.55, and exposed to 3.5% CaCl₂ solution

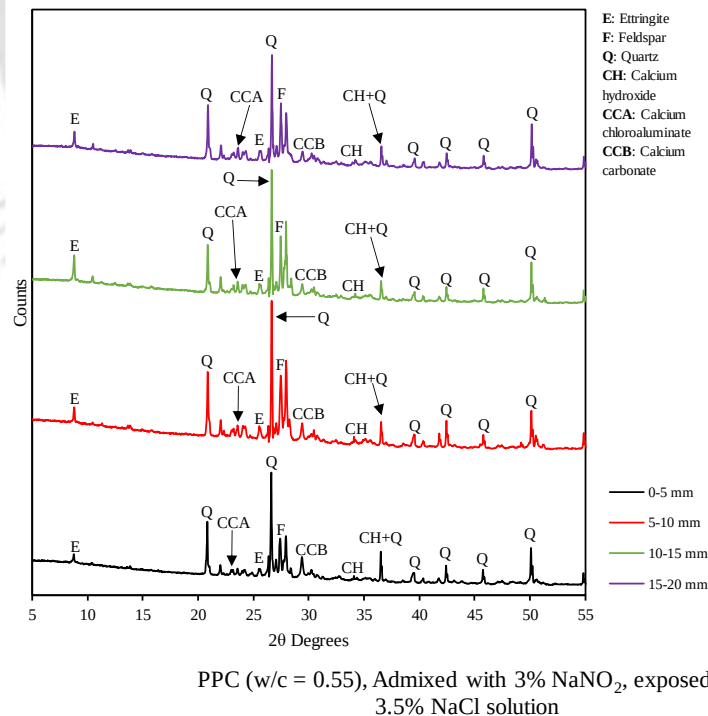


Fig. B53 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, and 15-20 mm from the exposure surface of PPC concrete admixed with 3% NaNO₂ at w/c of 0.55, and exposed to 3.5% NaCl solution

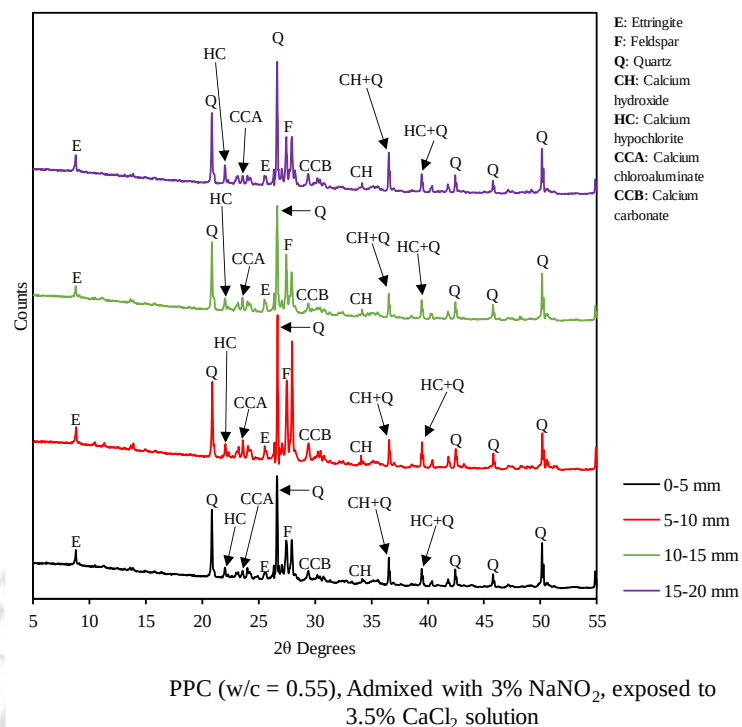


Fig. B54 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, and 15-20 mm from the exposure surface of PPC concrete admixed with 3% NaNO₂ at w/c of 0.55, and exposed to 3.5% CaCl₂ solution

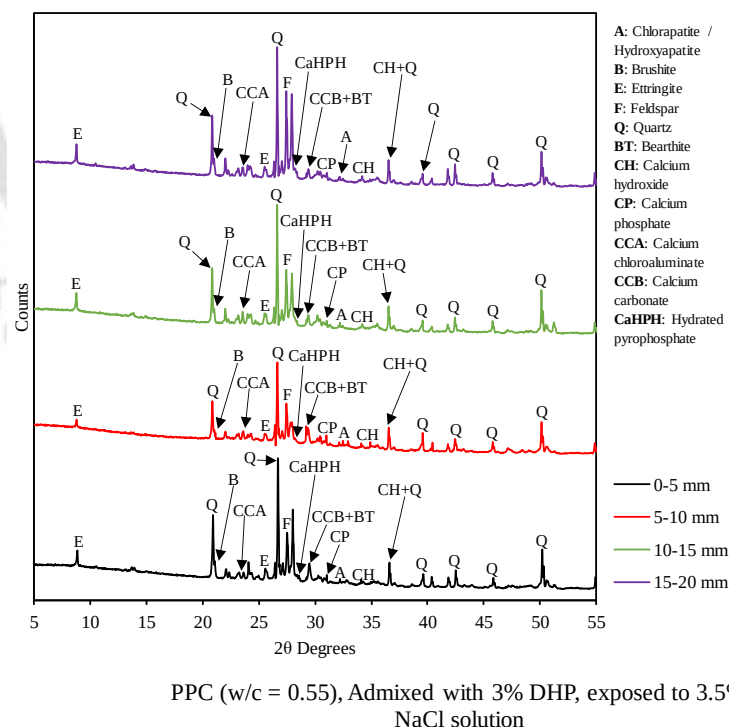
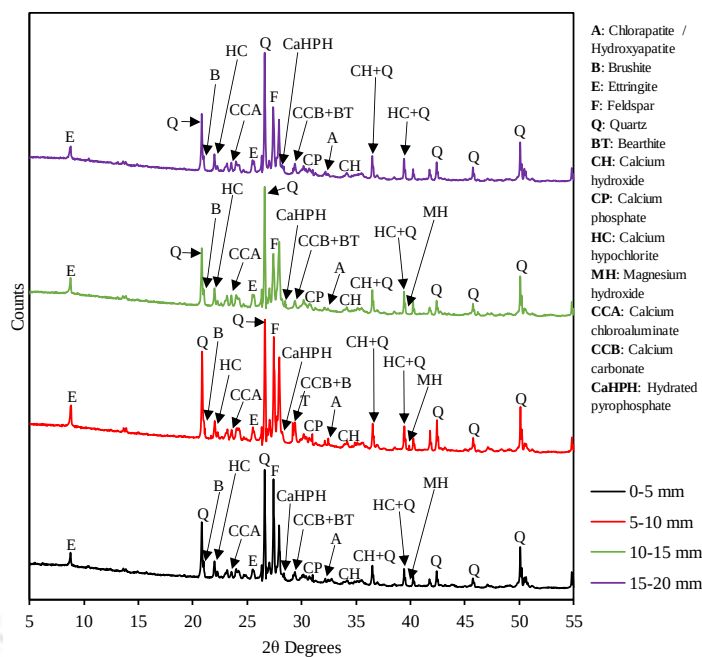


Fig. B55 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, and 15-20 mm from the exposure surface of PPC concrete admixed with 3% DHP at w/c of 0.55, and exposed to 3.5% NaCl solution



PPC (w/c = 0.55), Admixed with 3% DHP, exposed to 3.5% MgCl₂ solution

Fig. B56 XRD patterns at depth intervals of 0-5 mm, 5-10 mm, 10-15 mm, and 15-20 mm from the exposure surface of PPC concrete admixed with 3% DHP at w/c of 0.55, and exposed to 3.5% MgCl₂ solution

List of Publications

Publications from Ph.D. Thesis

Journals:

[1] J. K. Das and B. Pradhan, “Study on influence of nitrite and phosphate based inhibiting admixtures on chloride interaction, rebar corrosion, and microstructure of concrete subjected to different chloride exposures”, *Journal of Building Engineering*, Vol. 50, pp. 104192-1-20, 2022.

[2] J. K. Das and B. Pradhan, “Impact of cation type of chloride salts on diffusion behaviour and binding capacity of chloride ions in concrete containing sodium nitrite and disodium hydrogen phosphate”, *Journal of Materials in Civil Engineering*, ASCE, Vol. 34, pp. 04022013-1-26, 2022.

[3] J. K. Das and B. Pradhan, “Long term effect of corrosion inhibitor and associated cation type of chloride ions on chloride profile of concrete exposed to composite chloride-sulfate environment”, *Materials Today: Proceedings*, Vol. 32, pp. 803-809, 2020 #.

[4] J. K. Das and B. Pradhan, “Effect of cation type of chloride salts on corrosion behaviour of steel in concrete powder electrolyte solution in the presence of corrosion inhibitors”, *Construction and Building Materials*, Vol. 208, pp. 175-191, 2019.

Conferences:

[1] J. K. Das and B. Pradhan, “Chloride ingress and chloride binding in concrete admixed with corrosion inhibitor and exposed to chloride-sulfate solutions”, *Second ASCE India Conference on “Challenges of Resilient and Sustainable Infrastructure Development in Emerging Economies” (CRSIDE2020)*, Kolkata, India, March 2– 4, 2020.

[2] J. K. Das and B. Pradhan, “Long term effect of corrosion inhibitor and associated cation type of chloride ions on chloride profile of concrete exposed to composite chloride-sulfate environment”, *3rd International Conference on Innovative Technologies for Clean and Sustainable Development (ITCSD2020)*, Chandigarh, India, February 19 – 21, 2020.

[3] J. K. Das and B. Pradhan, “Effectiveness of corrosion inhibitors in chloride contaminated simulated concrete pore solution,” *Eighteenth National Congress on Corrosion Control, NCCI*, Chennai, India, February 24 – 26, pp.1-14, 2016.

Sl. No. [3] in the list of Journals is related to Sl. No. [2] in the list of Conferences.

Manuscript submitted/ to be submitted from Ph.D. Thesis

[1] J. K. Das and B. Pradhan, “Performance evaluation of inhibiting compounds against steel corrosion and chloride binding in concrete admixed with different chloride salts”, *Journal of Materials in Civil Engineering*, ASCE, 2022, (2nd review complete).

[2] J. K. Das and B. Pradhan, “Effect of corrosion inhibitors on corrosion behaviour of steel in concrete subjected to chloride and chloride-sulfate solutions”, *Journal of Materials in Civil Engineering*, ASCE, 2022 (To be submitted).

[3] J. K. Das and B. Pradhan, “Study on effect of chloride and composite chloride-sulfate exposure solutions on diffusion behaviour and binding capacity of chloride ions in concrete admixed with inhibiting compounds”, *Journal of Building Engineering*, 2022 (To be submitted).

Other Publications

Journals:

[1] N. S. Teklegiorgis, B. Pradhan, J. K. Prusty, and J. K. Das, “Effect of sodium nitrite as corrosion inhibitor against chloride-induced corrosion of steel rebar in geopolymer concrete containing fly ash and GGBS”, *Journal of Materials in Civil Engineering*, ASCE, Vol. 34, pp. 04022007-1-17, 2022.

Conferences:

[1] J. K. Das and B. Pradhan, “Effect of sodium nitrite on chloride-induced corrosion of steel in concrete”, *Recent Advancements in Construction Materials & Structures, ICCMS-2021*, Virtual mode, December 15– 17, 2021.

[2] F. A. Mekonnen, J. K. Das and B. Pradhan, “Performance evaluation of corrosion inhibitors against steel reinforcement corrosion in concrete subjected to internal chloride exposure”, *CORCON 2018*, Jaipur, India, September 30– October 3, 2018.

[3] Rozampua, J. K. Das and B. Pradhan, “A study on sodium nitrite, zinc oxide and disodium hydrogen phosphate as corrosion inhibitors in reinforced concrete”, *International Conference on Advances in Construction Materials and Systems (ICACMS2017)*, Chennai, India, September 3– 8, pp. 385-395, 2017.

[4] Rozampua, J. K. Das and B. Pradhan, “Performance of sodium nitrite and zinc oxide as corrosion inhibitors against chloride induced steel reinforcement corrosion in concrete”, *International Conference on Advances in Civil Engineering and Sustainable Construction, (ACESC2016)*, Chennai, India, March 30– April 1, pp. 59-65, 2016.