

Corrosion behavior of steel reinforcement in concrete exposed to composite chloride–sulfate environment

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HIGHLIGHTS

- Corrosion behavior of rebar in concrete was studied against various exposure solutions.
- Determination of corrosion parameters of rebar after exposure to composite solutions.
- Evaluation of effect of various parameters on rebar corrosion by analysis of variance.

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ABSTRACT

The corrosion of steel reinforcement in concrete is the most significant durability problem encountered in reinforced concrete structures. The concomitant presence of sulfate ions may affect chloride induced corrosion of steel reinforcement in concrete. In this paper the outcome of a comprehensive experimental investigation is presented wherein corrosion performance of steel reinforcement in concrete exposed to composite solutions of chloride and sulfate ions has been evaluated. In this investigation, concrete specimens with a centrally embedded steel bar have been prepared from two types of cement namely ordinary Portland cement (OPC) and Portland pozzolana cement (PPC), four w/c ratios and one type of steel reinforcement. The reinforced concrete specimens have been exposed to composite solutions of chloride and sulfate ions of different concentrations. Further in order to evaluate the effect of cation type associated with sulfate ions on corrosion parameters, sodium sulfate and magnesium sulfate were used individually with sodium chloride in the preparation of composite solutions. After exposure, the different corrosion parameters namely half-cell potential, relative resistivity and corrosion current density have been measured. From the results, it was observed that the specimens made with PPC exhibited higher values of relative resistivity and lower values of corrosion density as compared to those made with OPC in all the composite solutions. Further opposite behavior was observed between composite solutions of sodium chloride with magnesium sulfate and sodium chloride with sodium sulfate in terms of variations in relative resistivity and corrosion current density for both OPC and PPC. In addition on the basis of results of analysis of variance, the effect of different parameters on relative resistivity and corrosion current density in composite solutions of sodium chloride and magnesium sulfate and that in composite solutions of sodium chloride and sodium sulfate has also been evaluated.

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1. Introduction

Concrete is the most widely produced construction material on earth, with consumption, above dozens of billions of tons [1]. Dense concrete normally possesses excellent strength and durability properties. Because of this, concrete is most widely used for the construction of structures exposed to different types of environment varying from mild to severe. However as demand

for construction in harsh environments increases, the concern towards long service lives of reinforced concrete structures also increases [2]. Under mild environment the exposure conditions include concrete surfaces protected against weather or aggressive conditions; whereas the categories under severe environment include concrete surfaces exposed to severe rain, alternating wetting and drying or occasional freezing or severe condensation and concrete exposed to coastal environment [3]. The exposure conditions under extreme or harsh environment include surface of members in tidal zone, members in direct contact with liquid/solid aggressive chemicals such as chemical and radioactive waste

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3. Results and discussion

3.1. Compressive strength

As already stated, the 28 day compressive strength of concrete was determined in the compression testing machine. The compressive strength values of concrete made with OPC were found to be 37.63 N/mm², 34.96 N/mm², 29.78 N/mm² and 25.33 N/mm² at w/c ratios of 0.45, 0.50, 0.55 and 0.60 respectively. Similarly the compressive strength values of PPC concrete were 38.52 N/mm², 37.48 N/mm², 34.22 N/mm² and 27.41 N/mm² at w/c ratios of 0.45, 0.50, 0.55 and 0.60 respectively. From these results it is observed that concrete made with PPC showed higher compressive strength as compared to that made with OPC at all w/c ratios. This is due to the production of additional C–S–H gel by pozzolanic reaction in concrete mixes made with PPC. Further the compressive strength values decreased with increase in w/c ratio.

3.2. Potential value

The plot of half-cell potential values (with respect to saturated calomel electrode) of the steel bar embedded in the slab specimens and kept in laboratory exposure condition (control mix) at different w/c ratios for OPC and PPC is shown in Fig. 4. The half-cell potential values of the steel bar embedded in the slab specimens and exposed to composite solutions of chloride and sulfate ions at different w/c ratios are shown in Figs. 5–7 for specimens made with OPC and in Figs. 8–10 for specimens made with PPC. Similarly plots of half-cell potential vs. w/c ratio for specimens exposed to sodium chloride solution only are shown in Figs. 11 and 12 for OPC and PPC respectively. In these figures the terms ‘NC’, ‘MS’ and ‘NS’ represent sodium chloride, magnesium sulfate and sodium sulfate respectively. From these figures (Figs. 5–12) it is observed that, irrespective of cement type, w/c ratio, chloride ion concentration, sulfate ion concentration and associated cation type, the potential values were more negative than –270 mV (SCE)/–350 mV (Cu/CuSO₄ electrode), that corresponds to greater than 90% probability of occurrence of steel reinforcement corrosion as per ASTM C876 [30]. Thus it indicates initiation of steel reinforcement corrosion with greater probability in all exposure solutions. Further it is observed that there is no systematic variation in half-cell potential values with w/c ratio at different concentrations of chloride and sulfate ions (both magnesium sulfate and sodium sulfate) for both types of cement. It may be noted that potential values can be more negative than –270 mV (SCE)/–350 mV (Cu/CuSO₄ electrode) without significant presence of

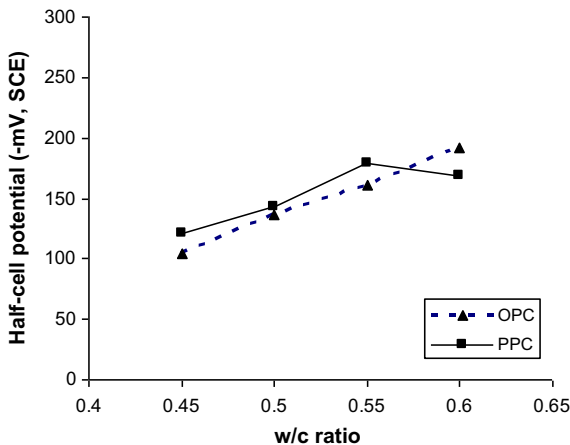


Fig. 4. Half-cell potential vs. w/c ratio in control concrete mix.

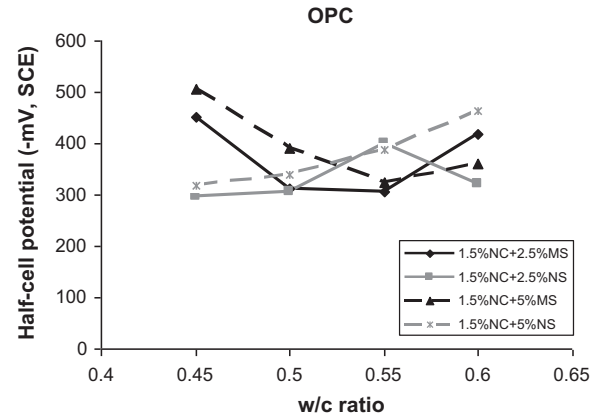


Fig. 5. Half-cell potential vs. w/c ratio for OPC exposed to composite solutions of sulfate ions (MgSO₄ and Na₂SO₄) with 1.5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

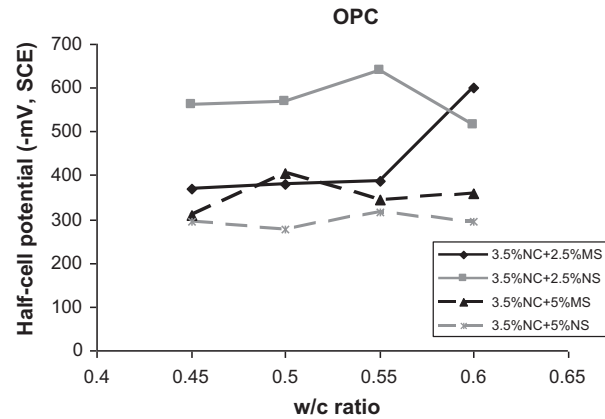


Fig. 6. Half-cell potential vs. w/c ratio for OPC exposed to composite solutions of sulfate ions (MgSO₄ and Na₂SO₄) with 3.5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

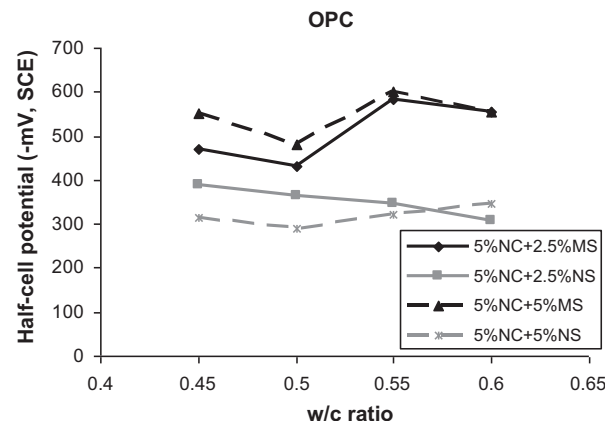


Fig. 7. Half-cell potential vs. w/c ratio for OPC exposed to composite solutions of sulfate ions (MgSO₄ and Na₂SO₄) with 5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

corrosion and this is due to polarization phenomena induced by limited oxygen diffusion [1,10]. Thus potential values may not be sufficient to evaluate the corrosion behavior. In control mix, the potential values were more positive than –270 mV (SCE) for both types of cement and at all w/c ratios as observed from Fig. 4. This

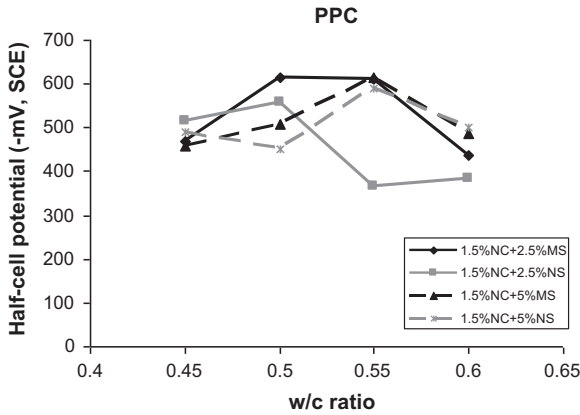


Fig. 8. Half-cell potential vs. *w/c* ratio for PPC exposed to composite solutions of sulfate ions ($MgSO_4$ and Na_2SO_4) with 1.5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

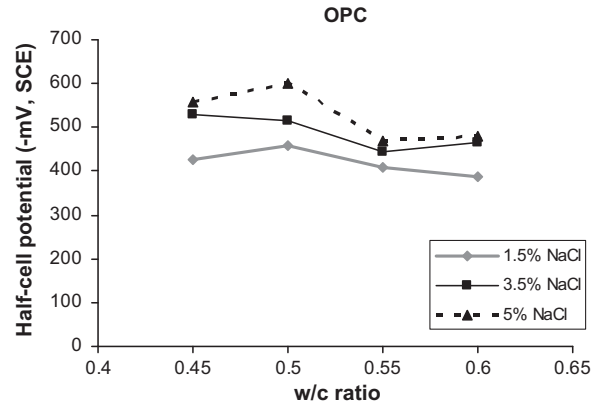


Fig. 11. Half-cell potential vs. *w/c* ratio for OPC exposed to sodium chloride solutions.

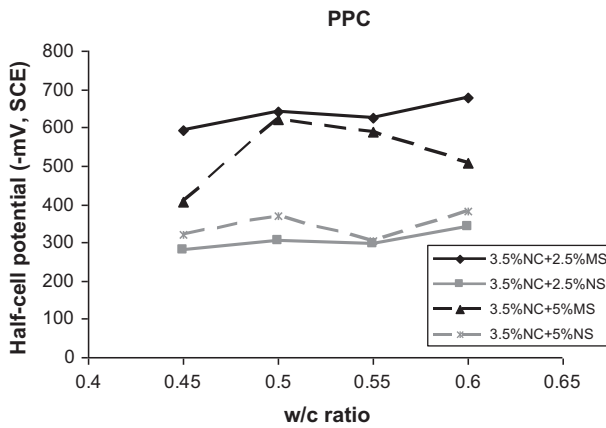


Fig. 9. Half-cell potential vs. *w/c* ratio for PPC exposed to composite solutions of sulfate ions ($MgSO_4$ and Na_2SO_4) with 3.5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

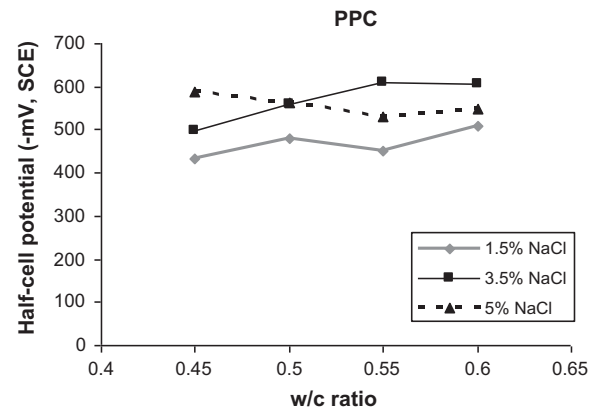


Fig. 12. Half-cell potential vs. *w/c* ratio for PPC exposed to sodium chloride solutions.

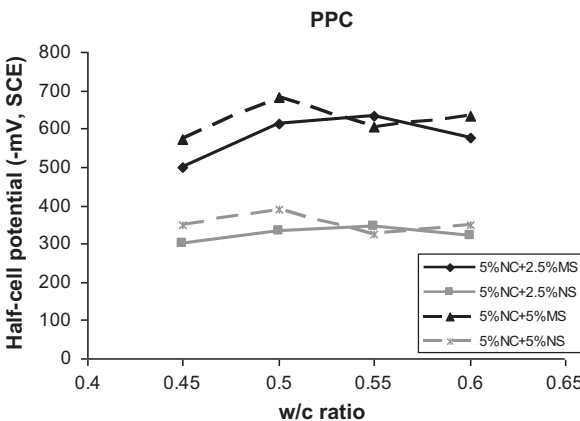


Fig. 10. Half-cell potential vs. *w/c* ratio for PPC exposed to composite solutions of sulfate ions ($MgSO_4$ and Na_2SO_4) with 5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

indicates lower probability of occurrence of steel reinforcement corrosion in the control mix. From Figs. 5–10 it is inferred that, the specimens exposed to composite solutions of sodium chloride and sodium sulfate mostly exhibited less negative potential as compared to those exposed to composite solutions of sodium

chloride and magnesium sulfate for both types of cement. It may be due to the reduction in concentration of iron ions in the electrolytic pore solution of the concrete [12], which is exposed to composite solutions of sodium chloride and sodium sulfate. The half-cell potential values mostly decreased with increase in sodium chloride concentration for both types of cement as observed from Figs. 11 and 12.

3.3. Relative resistivity

The measured IR compensation value which is obtained by dividing the IR drop value across the cover concrete within the confined area of the guard ring with the corrosion current density represents the relative resistivity of the cover concrete. The IR compensation values of the specimens exposed to different solutions and also of control mix were determined at the age of three hundred days. The plot of relative resistivity (in Ωcm^2) of specimens kept in laboratory exposure condition (control mix) at different *w/c* ratios for OPC and PPC is shown in Fig. 13. The plots of relative resistivity (in Ωcm^2) of concrete exposed to composite solutions of chloride and sulfate ions at different *w/c* ratios are presented in Figs. 14–16 for specimens made with OPC and in Figs. 17–19 for specimens made with PPC. From these figures it is observed that the resistivity values mostly increased with decrease in *w/c* ratio for both types of cement in control mix and also in the specimens subjected to exposure solutions. In few cases, higher value of relative resistivity was observed at higher *w/c* ratio as compared to that at lower *w/c* ratio. This may be possibly due to

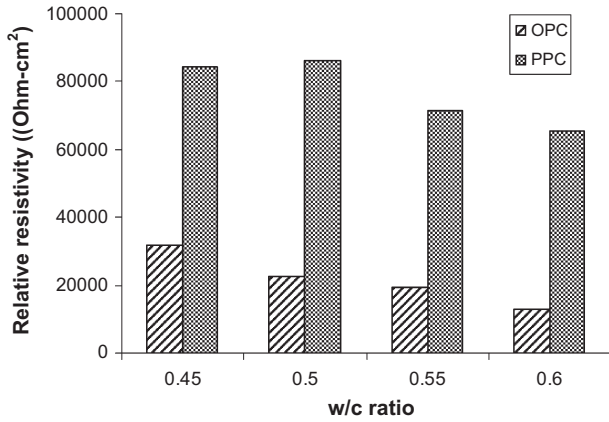


Fig. 13. Relative resistivity of control mix for OPC and PPC at different w/c ratios.

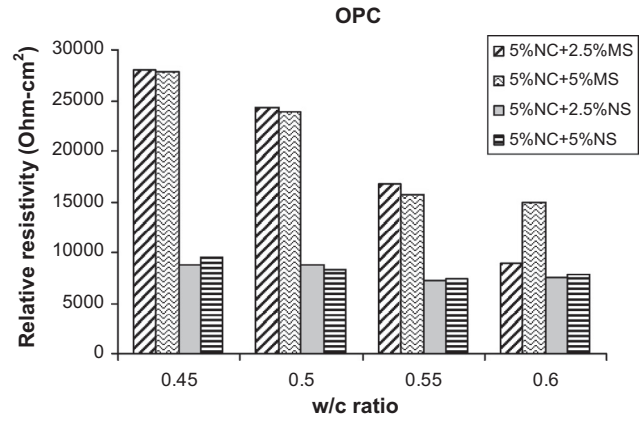


Fig. 16. Relative resistivity at different w/c ratios for OPC exposed to composite solutions of sulfate ions ($MgSO_4$ and Na_2SO_4) with 5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

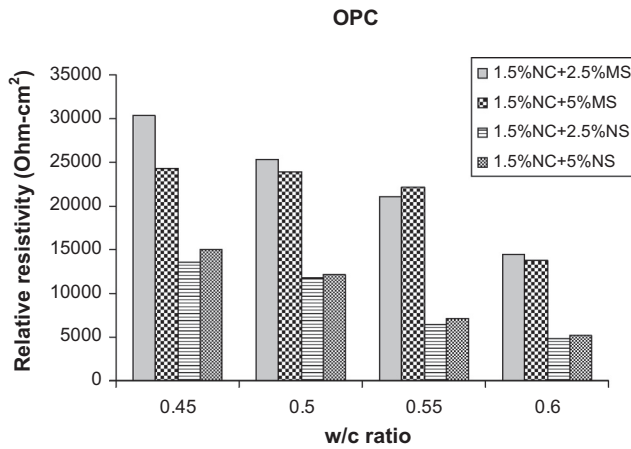


Fig. 14. Relative resistivity at different w/c ratios for OPC exposed to composite solutions of sulfate ions ($MgSO_4$ and Na_2SO_4) with 1.5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

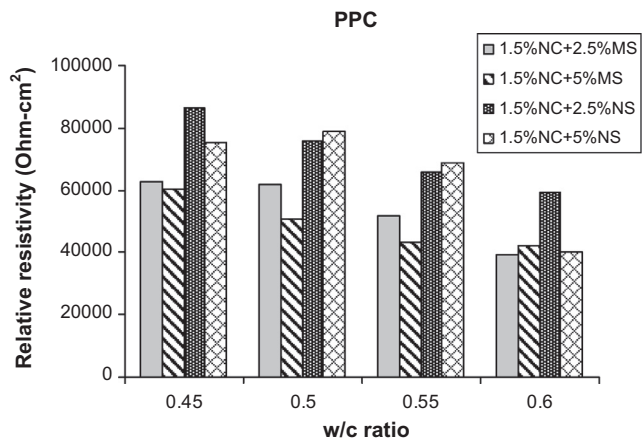


Fig. 17. Relative resistivity at different w/c ratios for PPC exposed to composite solutions of sulfate ions ($MgSO_4$ and Na_2SO_4) with 1.5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

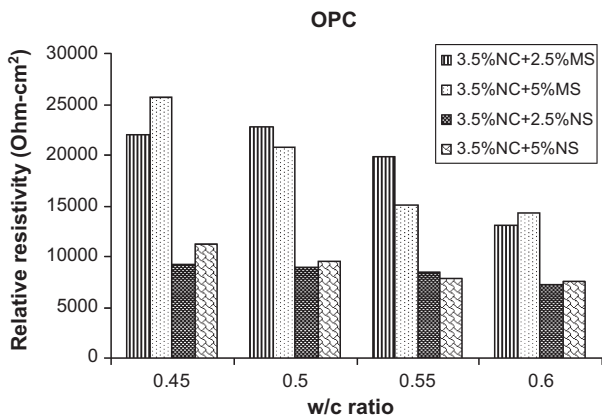


Fig. 15. Relative resistivity at different w/c ratios for OPC exposed to composite solutions of sulfate ions ($MgSO_4$ and Na_2SO_4) with 3.5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

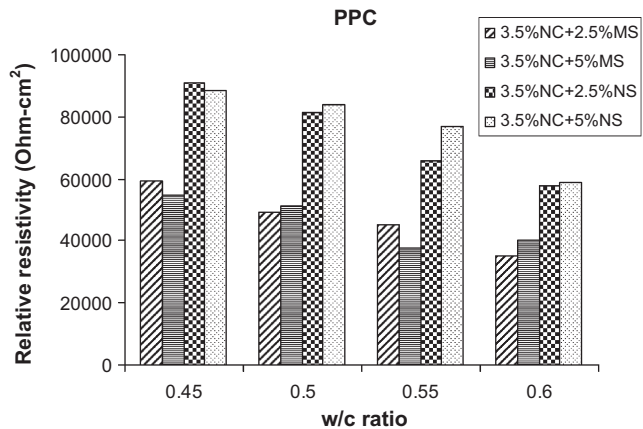


Fig. 18. Relative resistivity at different w/c ratios for PPC exposed to composite solutions of sulfate ions ($MgSO_4$ and Na_2SO_4) with 3.5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

lower moisture content in the cover concrete at higher w/c ratio as compared to that at lower w/c ratio and as concrete is a heterogeneous composite, this local alteration in moisture content might have resulted in a increase in concrete resistivity at higher w/c ratio than that at lower w/c ratio. As observed from Table 1, the

cement-to-aggregate ratio decreases with increase in w/c ratio. The concrete mix made with lower w/c ratio exhibits denser microstructure due to production of more C–S–H gel as result of higher cement content as compared to the concrete mix made with higher

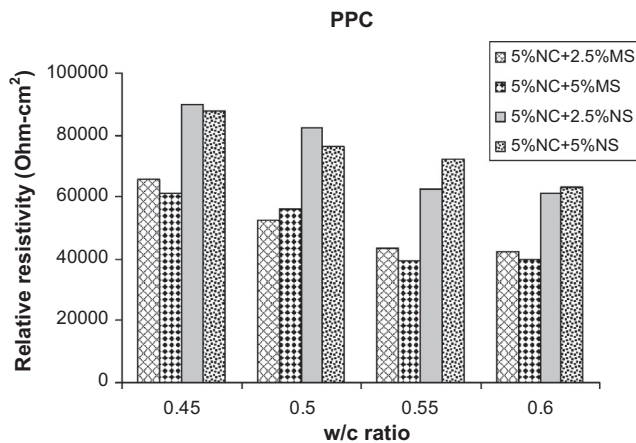


Fig. 19. Relative resistivity at different w/c ratios for PPC exposed to composite solutions of sulfate ions ($MgSO_4$ and Na_2SO_4) with 5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

w/c ratio. Due to the difference in denseness of microstructure, the penetration of chloride ions and sulfate ions into concrete is different at different w/c ratios. This is reflected in the values of relative resistivity of concrete, as specimens made with lower w/c ratio exhibited higher values of relative resistivity as compared to those made with higher w/c ratios. Further the specimens made with PPC showed higher value of relative resistivity as compared to those made with OPC in all exposure solutions and also in control mix. This is due to formation of denser microstructure as result of production of additional C–S–H gel due to pozzolanic reaction in concrete made with PPC as compared to that made with OPC and thus lowering the penetration of aggressive ions in the concrete made with PPC. On comparison between control mix and those exposed to composite chloride–sulfate solutions, it is observed that there is no systematic variation in of relative resistivity values. This may attributed to the effect of variation in moisture content in control mix and in the specimens exposed to these solutions; and also due to the effect of formation of expansive products in the specimens exposed to these solution, thereby altering the resistivity of concrete.

From Figs. 14–16, it is observed that the OPC specimens exposed to magnesium sulfate solutions exhibited higher values of relative resistivity as compared to those exposed to sodium sulfate solutions at all concentrations of sodium chloride and at all w/c ratios incorporated in the study. However the opposition was observed for specimens made from PPC, i.e. PPC specimens subjected to sodium sulfate solutions showed higher values of relative resistivity as compared to those subjected to magnesium sulfate solutions at all chloride concentrations as observed from Figs. 17–19. This may be attributed to the fact that for OPC specimens exposed to composite solutions of sodium chloride and magnesium sulfate, there is comparatively higher production of magnesium hydroxide (brucite) due to the reaction between calcium hydroxide (portlandite) and magnesium sulfate and thus resulting in higher resistivity due to filling of pores with magnesium hydroxide. It may be noted here that, calcium hydroxide acts as the first defensive material to react with magnesium sulfate [31] and thus act as retarder to the attack of magnesium and sulfate ions on C–S–H gel. Rasheeduzzafar et al. [32] have carried out XRD and SEM analysis on cement paste specimens after an exposure of 2 years in mixed magnesium–sodium sulfate solutions. The results of XRD and SEM analysis indicated the formation of brucite in ordinary Portland cement whereas relatively marginal quantity of brucite was formed in fly ash blended cement. Further, XRD and SEM analysis from this study also indicated the reduction in

portlandite in plain and blended cements due to formation of gypsum. For OPC specimens exposed to composite solutions of sodium chloride and sodium sulfate (Figs. 14–16), formation of more amount of gypsum and ettringite might have resulted in lower relative resistivity as result of less denser microstructure. For PPC specimens exposed to composite solutions of sodium chloride and magnesium sulfate (Figs. 17–19), the lower relative resistivity may be attributed to the decrease in calcium hydroxide (that acts as the first defensive material to react with magnesium sulfate) content as a result of consumption in pozzolanic reaction and due to formation of gypsum. Due to reduction in calcium hydroxide content in PPC, the reaction of magnesium and sulfate ions with C–S–H gel leads to the formation of gypsum and non-cementitious M–S–H (magnesium silicate hydrate) [31] and this effect is possibly more dominant than more production of C–S–H gel and thereby lowering the relative resistivity of concrete. Similarly for specimens made from PPC and subjected to composite solutions of sodium chloride and sodium sulfate (Figs. 17–19), the higher relative resistivity may be due to reduction in the formation of gypsum and ettringite due to less availability of calcium hydroxide and C_3A respectively in PPC and due to formation of denser structure as result of production of additional C–S–H gel due to pozzolanic reaction [31].

The variation in relative resistivity with sulfate ion concentration is mostly not systematic in both types of composite solutions as observed Figs. 14–19. The plots of relative resistivity of concrete specimens exposed to chloride solution only are shown in Figs. 20 and 21 for OPC and PPC respectively. From Fig. 20, it is noted that for OPC, the resistivity mostly decreased with increase in chloride ion concentration. For PPC, mostly there was no systematic variation in relative resistivity with chloride ion concentration as observed from Fig. 21, however highest and lowest value of resistivity were observed at exposure to sodium chloride concentrations of 1.5% and 5% respectively. From Figs. 14–16 and 20, it is observed that the OPC specimens exposed to composite solutions of sodium chloride and magnesium sulfate showed higher values of relative resistivity as compared to those exposed to only sodium chloride solution. However opposition was observed in case of OPC specimens exposed to composite solutions of sodium chloride and sodium sulfate, i.e. resistivity was more in specimens subjected to sodium chloride solution only as compared to that in composite solutions of sodium chloride and sodium sulfate. In composite solutions of sodium chloride and magnesium sulfate, the presence of chloride ions may not have affected the formation of brucite significantly at all concentrations of sodium chloride used in the study and thus exhibiting higher relative resistivity in OPC specimens as compared to that in only sodium chloride solution

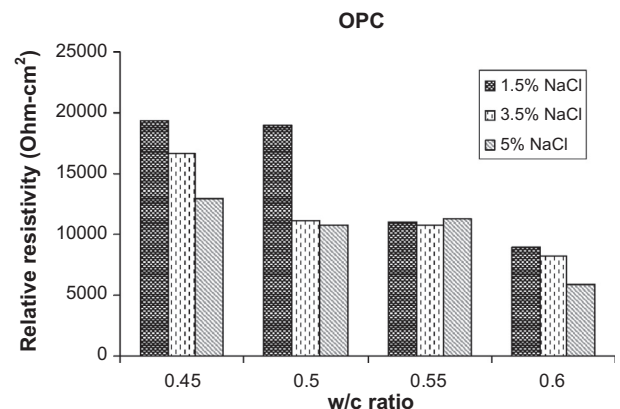


Fig. 20. Relative resistivity at different w/c ratios for OPC exposed to sodium chloride solutions.

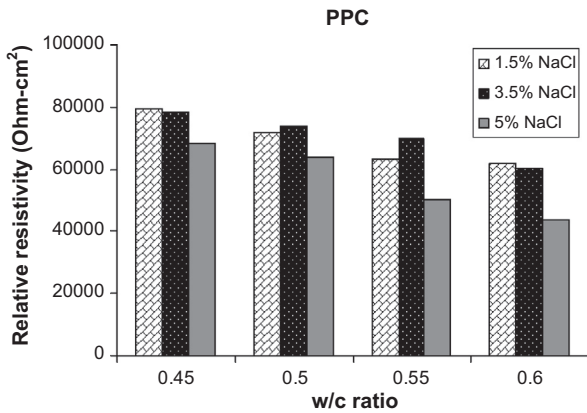


Fig. 21. Relative resistivity at different w/c ratios for PPC exposed to sodium chloride solutions.

wherein the presence of chloride ions increased the conductivity of concrete, thereby lowering the relative resistivity of concrete. The lower resistivity of OPC specimens in composite solutions of sodium chloride and sodium sulfate as compared to that in chloride solution only may be due to increase in conductivity of concrete in the presence of chloride ions along with the formation of gypsum and ettringite.

From Figs. 17–19 and 21, it is noted that the PPC specimens in composite solutions of sodium chloride and sodium sulfate mostly showed higher values of relative resistivity as compared to those exposed to only sodium chloride solution whereas the PPC specimens in composite solutions of sodium chloride and magnesium sulfate showed lower values of relative resistivity as compared to those exposed to only sodium chloride solution. This is due to the fact that the effect of formation of additional C–S–H gel was more dominant than the increase in conductivity of concrete in the presence of chloride ions, thereby resulting in higher resistivity for PPC in composite solutions of sodium chloride and sodium sulfate as compared to that exposed to only sodium chloride solution. The lower resistivity of PPC in composite solutions of sodium chloride and magnesium sulfate as compared to that in only sodium chloride solution is attributed to the combined effect of formation of gypsum and non-cementitious magnesium silicate hydrate along with the effect of conductivity in the presence of chloride ions, thereby lowering the relative resistivity.

3.4. Corrosion current density

The plot of corrosion current density (in $\mu\text{A}/\text{cm}^2$) of the specimens kept in laboratory exposure condition (control mix) at different w/c ratios for OPC and PPC is shown in Fig. 22. The results of corrosion current density of steel reinforcement in the specimens exposed to composite solutions of chloride and sulfate ions at different w/c ratios are shown in Figs. 23–25 for OPC concrete specimens and in Figs. 26–28 for specimens made with PPC. Further the plots of corrosion current density at different w/c ratios for specimens exposed to sodium chloride solution only are shown in Figs. 29 and 30 for OPC and PPC specimens respectively. From the obtained results it was observed that, the difference in corrosion current density values between the average value of three replicates and the individual replicate value of the same concrete mix is little. The same was also observed in half-cell potential and relative resistivity values.

From Figs. 22–30, it is found that the specimens made from PPC showed lower values of corrosion current density as compared to those made from OPC in all exposure solutions and at all w/c ratios.

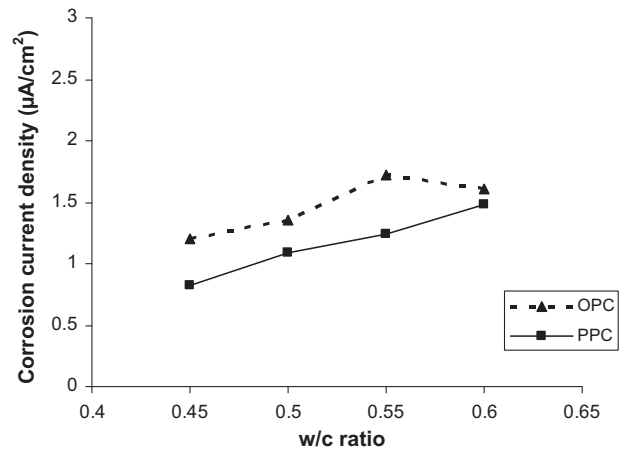


Fig. 22. Corrosion current density in control mix for both types of cement and different w/c ratios.

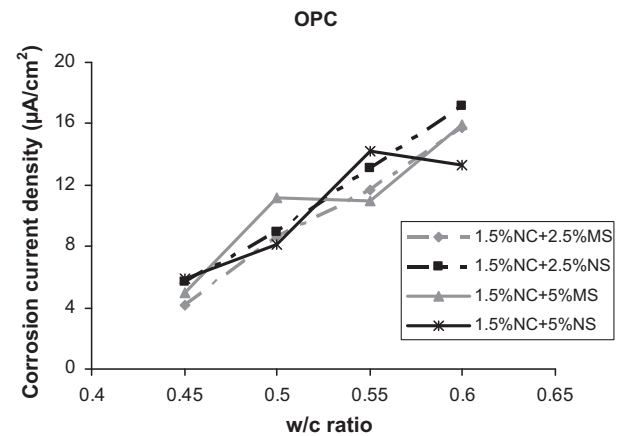


Fig. 23. Corrosion current density vs. w/c ratio for OPC exposed to composite solutions of sulfate ions (MgSO_4 and Na_2SO_4) with 1.5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

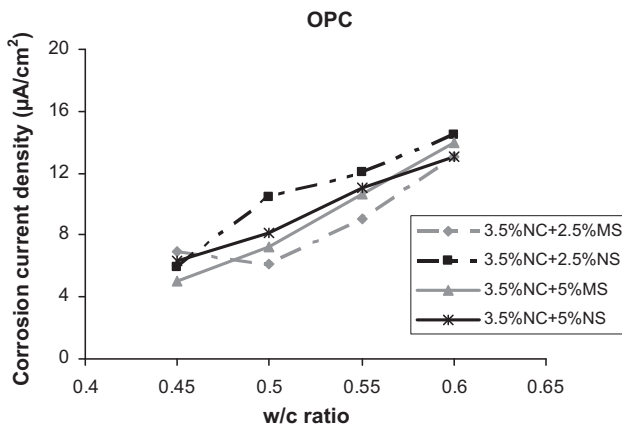


Fig. 24. Corrosion current density vs. w/c ratio for OPC exposed to composite solutions of sulfate ions (MgSO_4 and Na_2SO_4) with 3.5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

This is due to the formation of denser microstructure in the specimens made with PPC than that in OPC, thus resulting in higher resistivity of concrete and significantly retarding the diffusion of

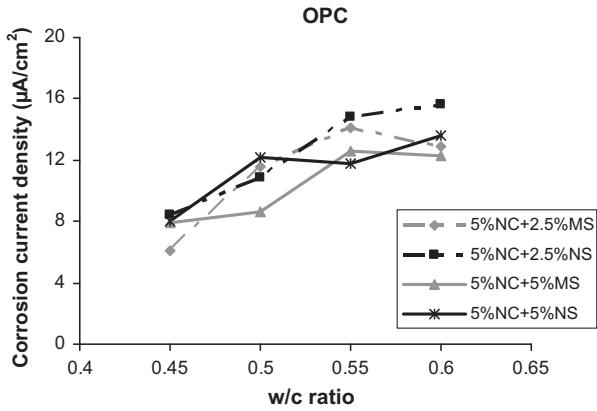


Fig. 25. Corrosion current density vs. w/c ratio for OPC exposed to composite solutions of sulfate ions ($MgSO_4$ and Na_2SO_4) with 5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

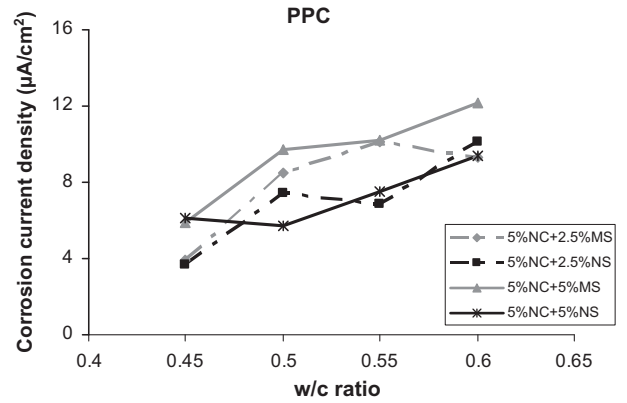


Fig. 28. Corrosion current density vs. w/c ratio for PPC exposed to composite solutions of sulfate ions ($MgSO_4$ and Na_2SO_4) with 5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

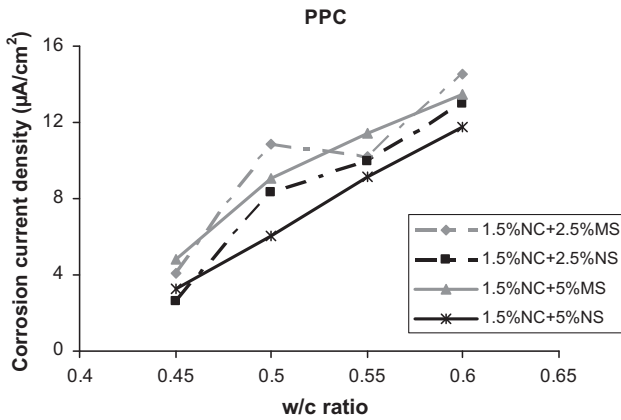


Fig. 26. Corrosion current density vs. w/c ratio for PPC exposed to composite solutions of sulfate ions ($MgSO_4$ and Na_2SO_4) with 1.5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

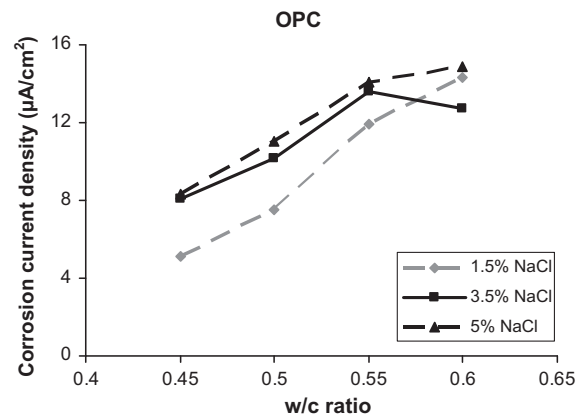


Fig. 29. Corrosion current density vs. w/c ratio for OPC exposed to sodium chloride solutions.

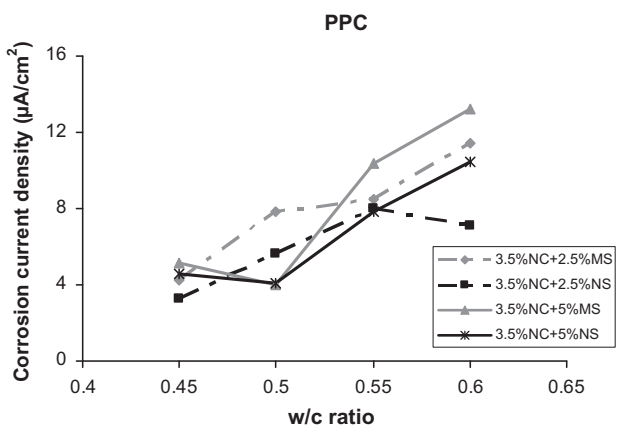


Fig. 27. Corrosion current density vs. w/c ratio for PPC exposed to composite solutions of sulfate ions ($MgSO_4$ and Na_2SO_4) with 3.5% sodium chloride (NC: sodium chloride, MS: magnesium sulfate and NS: sodium sulfate).

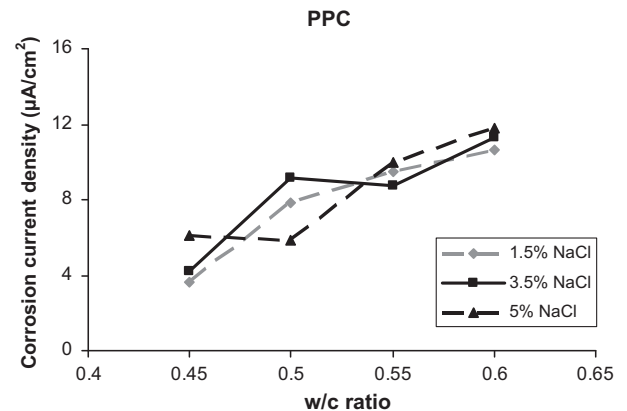


Fig. 30. Corrosion current density vs. w/c ratio for PPC exposed to sodium chloride solutions.

oxygen to the steel reinforcement level in concrete. On an average, corrosion current density of OPC specimens was about 1.01–1.43 times that of PPC specimens in composite solutions of sodium chloride and magnesium sulfate whereas in composite solutions of sodium chloride and sodium sulfate, corrosion current density of OPC specimens was about 1.46–1.87 times that of PPC

specimens. Further it is observed that the corrosion current density mostly increased with increase in w/c ratio in different exposure solutions for both types of cement. However the variation was not as systematic as that for relative resistivity with w/c ratio. In some cases the opposite trend in corrosion current density was observed at different w/c ratios. This opposite trend is possibly due to the alteration in moisture content in the cover concrete that might have changed the conductivity of concrete. As concrete is a

heterogeneous material, this local alteration in conductivity of concrete might have resulted in an opposite variation in corrosion current density values at these w/c ratios.

From Figs. 29 and 30, it is inferred that corrosion current density values increased with increase in sodium chloride concentration in both types of cement and this is due to increase in conductivity of concrete in the presence of higher amount of chloride ions at the rebar level. On comparison of corrosion current density between control concrete mix and those exposed to chloride and composite chloride–sulfate solutions, it is observed that control mix specimens exhibited lower values of corrosion current density as compared those subjected to various exposure solutions.

From Figs. 23–25, it is observed that the OPC specimens exposed to composite solutions of sodium chloride and magnesium sulfate mostly showed lower values of corrosion current density as compared to those exposed to composite solutions of sodium chloride and sodium sulfate. This is attributed to increase in resistivity of OPC concrete in composite solutions of sodium chloride and magnesium sulfate due to filling of pores with magnesium hydroxide as compared to lower resistivity of OPC in composite solutions of sodium chloride and sodium sulfate due to formation of more amount of gypsum and ettringite.

From Figs. 26–28, it is found that specimens made with PPC mostly exhibited lower values of corrosion current density in composite solutions of sodium chloride and sodium sulfate as compared to those exposed to composite solutions of sodium chloride and magnesium sulfate. The lower corrosion current density of PPC in composite solutions of sodium chloride and sodium sulfate may be due to higher resistivity as result of reduction in formation of gypsum and ettringite as compared to lower resistivity of PPC concrete in composite solutions of sodium chloride and magnesium sulfate due to the formation gypsum and non-cementitious magnesium silicate hydrate.

Further From Figs. 23–25 and 29, it is observed that, OPC specimens exposed to composite solutions of sodium chloride and magnesium sulfate mostly showed lower values of corrosion current density as compared to those exposed to only sodium chloride solution. However opposition was observed for OPC specimens exposed to composite solutions of sodium chloride and sodium sulfate, i.e. corrosion current density was mostly higher in specimens subjected to composite solutions of sodium chloride and sodium sulfate as compared to that in only sodium chloride solution. From Figs. 26–28 and 30, it is found that the PPC specimens in composite solutions of sodium chloride and magnesium sulfate mostly showed higher values of corrosion current density

as compared to that in only sodium chloride solution whereas PPC specimens in composite solutions of sodium chloride and sodium sulfate mostly resulted in lower values of corrosion current density as compared to those exposed to only sodium chloride solution. The variations in corrosion current density in specimens made with both OPC and PPC in above exposure solutions are due to variations in resistivity of concrete and the reasons for variations in resistivity of concrete in different exposure solutions are already stated earlier. Further it is noted that there is no systematic variation in corrosion current density with concentration of sulfate ions incorporated in the study for both types of composite solutions.

From the aforementioned discussions on obtained results, it is observed that the relative resistivity and corrosion current density of steel in concrete specimens subjected to different exposure solutions varied with w/c ratio as the ingress of chloride ions and sulfate ions varied depending on the permeability of concrete. Thus the extent of reactions taking place on the steel surface in the presence of chloride ions and the change in microstructure of concrete due to the reactions of chloride and sulfate ions with hydrated cement products may be affected by the extent of penetration of these ions, which is influenced by permeability of concrete that depends on w/c ratio. In some cases, opposite trend in relative resistivity and corrosion current density was observed at different w/c ratios in different exposure solutions.

The results of corrosion parameters obtained from this investigation provide information about the corrosion behavior of reinforced concrete exposed to external chloride and composite chloride–sulfate solutions of known concentrations for a certain period of time.

3.5. Analysis of variance for relative resistivity and corrosion current density

For the purpose of analyzing the effect of different factors on the variation of relative resistivity and corrosion current density of steel reinforcement in concrete exposed to composite solutions of different concentrations of chloride and sulfate ions, the analysis of variance (ANOVA) calculation was carried out as per the guidelines presented by Hicks [33]. The relative resistivity and corrosion current density values of specimens for two types of cement, four w/c ratios at different concentrations of sodium chloride and magnesium sulfate and those at different concentrations of sodium chloride and sodium sulfate were tabulated separately for relative resistivity and corrosion current density. The total sum of squares was calculated, which is divided into the sum of squares (SS) for individual factors and that for the residual random error. Mean

Table 3a
Analysis of variance results for relative resistivity in composite solutions of sodium chloride and magnesium sulfate.

Source	Level	Degree of freedom (df)	Sum of squares (SS)	Mean squares (MS)	F-ratio	'F' from Fisher's distribution at 95% probability
Cement type	2	1	1.013×10^{10}	1.013×10^{10}	871.145	4.08
w/c ratio	4	3	2.077×10^9	6.923×10^8	59.535	2.84
Chloride ion concentration	3	2	1.178×10^8	5.891×10^7	5.066	3.23
Sulfate ion concentration	2	1	2.856×10^7	2.856×10^7	2.456	4.08
Error		40	4.652×10^8	1.163×10^7		
Total		47	1.282×10^{10}			

Table 3b
Analysis of variance results for relative resistivity in composite solutions of sodium chloride and sodium sulfate.

Source	Level	Degree of freedom (df)	Sum of squares (SS)	Mean squares (MS)	F-ratio	'F' from Fisher's distribution at 95% probability
Cement type	2	1	4.936×10^{10}	4.936×10^{10}	1117.976	4.08
w/c ratio	4	3	2.053×10^9	6.843×10^8	15.497	2.84
Chloride ion concentration	3	2	7.286×10^7	3.643×10^7	0.825	3.23
Sulfate ion concentration	2	1	1.501×10^5	1.501×10^5	0.003	4.08
Error		40	1.766×10^9	4.416×10^7		
Total		47	5.326×10^{10}			

Table 4a

Analysis of variance results for corrosion current density in composite solutions of sodium chloride and magnesium sulfate.

Source	Level	Degree of freedom (df)	Sum of squares (SS)	Mean squares (MS)	F-ratio	'F' from Fisher's distribution at 95% probability
Cement type	2	1	16.532	16.532	7.231	4.08
w/c ratio	4	3	406.862	135.621	59.319	2.84
Chloride ion concentration	3	2	21.40	10.70	4.68	3.23
Sulfate ion concentration	2	1	1.138	1.138	0.498	4.08
Error		40	91.452	2.286		
Total		47	537.384			

Table 4b

Analysis of variance results for corrosion current density in composite solutions of sodium chloride and sodium sulfate.

Source	Level	Degree of freedom (df)	Sum of squares (SS)	Mean squares (MS)	F-ratio	'F' from Fisher's distribution at 95% probability
Cement type	2	1	174.159	174.159	89.360	4.08
w/c ratio	4	3	342.943	114.314	58.654	2.84
Chloride ion concentration	3	2	14.454	7.227	3.708	3.23
Sulfate ion concentration	2	1	3.040	3.040	1.560	4.08
Error		40	77.958	1.949		
Total		47	612.554			

squares (MS) of the factors were then calculated by dividing their corresponding sum of squares by the associated degrees of freedom (df). The effect of individual factors on relative resistivity and corrosion current density was then estimated by testing the hypothesis of equality of variances, which is the test of null hypothesis or simply the significance test at a particular probability level. For obtaining this, the *F*-statistic which is the ratio of mean squares of different factors to the mean squares of the residual error was calculated and then compared with the tabulated *F*-values related to Fisher distribution. The *F*-values related to Fisher distribution depending on number of degrees of freedom of individual factors and that of residual error at a probability level are available in relevant texts [33]. The results of analysis of variance for relative resistivity for composite solutions of sodium chloride and magnesium sulfate and that for composite solutions of sodium chloride and sodium sulfate are presented in Tables 3a and 3b respectively. Similarly the results of analysis of variance for corrosion current density are presented in Tables 4a and 4b for composite solutions of sodium chloride and magnesium sulfate and sodium chloride and sodium sulfate respectively. From Tables 3a and 4a, it is observed that, all the factors except concentration of sulfate ions are affecting both relative resistivity and corrosion current density in composite solutions of sodium chloride and magnesium sulfate, as the estimated *F*-values are higher than the tabulated *F*-values at 95% confidence level. Further from Table 3b, it is inferred that cement type and w/c ratio are only affecting relative resistivity of concrete in composite solutions of sodium chloride and sodium sulfate whereas all the factors except concentration of sulfate ions are affecting corrosion current density as observed from Table 4b.

4. Conclusions

From the results of the present study, the following conclusions were obtained;

- (i) The half-cell potential values were more negative than -270 mV (SCE)/ -350 mV (Cu/CuSO₄ electrode) for both types of cement at all w/c ratios and in all exposure solutions, thus indicating the initiation of steel reinforcement corrosion in concrete.
- (ii) The specimens made with PPC exhibited higher values of relative resistivity and lower values of corrosion density as compared to those made with OPC in all exposure solutions at all w/c ratios.

- (iii) The specimens made with OPC showed higher values of relative resistivity and lower values of corrosion current density in composite solutions of sodium chloride and magnesium sulfate whereas opposite behavior was observed for OPC in composite solutions of sodium chloride and sodium sulfate.
- (iv) PPC exhibited lower values of relative resistivity and higher values of corrosion density when exposed to composite solutions of sodium chloride and magnesium sulfate whereas it showed opposite behavior in composite solutions of sodium chloride and sodium sulfate.
- (v) The variations in relative resistivity and corrosion current density between composite solutions of sodium chloride with magnesium sulfate and sodium chloride solution; and that between composite solutions of sodium chloride with sodium sulfate and sodium chloride solution were mostly opposite for both OPC and PPC.
- (vi) From the results of analysis of variance it is found that except concentration of sulfate ions; cement type, w/c ratio and chloride ion concentration are affecting both relative resistivity and corrosion current density in composite solutions of sodium chloride and magnesium sulfate. In composite solutions of sodium chloride and sodium sulfate, chloride ions and sulfate ions did not have significant effect on the variations in relative resistivity, however chloride ion concentration along with cement type and w/c ratio have significant effect on corrosion current density of steel in concrete.

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References

- [1] Montemor MF, Simoes AMP, Ferreira MGS. Chloride-induced corrosion on reinforcing steel: from the fundamentals to the monitoring techniques. *Cem Concr Compos* 2003;25:491–502.
- [2] Monteiro PJM, Kurtis KE. Time to failure for concrete exposed to severe sulfate attack. *Cem Concr Res* 2003;2003(33):987–93.
- [3] IS 456-2000. Plain and reinforced concrete – code of practice. New Delhi: Bureau of Indian Standards.
- [4] Li CQ, Zheng JJ, Lawanwisut W, Melchers RE. Concrete delamination caused by steel reinforcement corrosion. *J Mater Civ Eng ASCE* 2007;19:591–600.

- [5] Alhozaimey A, Hussain RR, Al-Zaid R, Al Negheimish A. Investigation of severe corrosion observed at intersection points of steel rebar mesh in reinforced concrete construction. *Constr Build Mater* 2012;37:67–81.
- [6] Saricimen H, Mohammad M, Quddus A, Shameem M, Barry MS. Effectiveness of concrete inhibitors in retarding rebar corrosion. *Cem Concr Compos* 2002;24:89–100.
- [7] Dehwah HAF, Maslehuddin M, Austin SA. Long-term effect of sulfate ions and associated cation type on chloride-induced reinforcement corrosion in Portland cement concretes. *Cem Concr Compos* 2002;24:17–25.
- [8] Arya C, Xu Y. Effect of cement type on chloride binding and corrosion of steel in concrete. *Cem Concr Res* 1995;25:893–902.
- [9] Santhanam M, Cohen M, Olek J. Differentiating seawater and groundwater sulfate attack in Portland cement mortars. *Cem Concr Res* 2006;36:2132–7.
- [10] Choi YS, Kim JG, Lee KM. Corrosion behavior of steel bar embedded in fly ash concrete. *Corros Sci* 2006;48:1733–45.
- [11] Al-Akhras NM. Durability of metakaolin concrete to sulfate attack. *Cem Concr Res* 2006;36:1727–34.
- [12] Pradhan B, Bhattacharjee B. Role of steel and cement type on chloride induced corrosion in concrete. *ACI Mater J* 2007;104:612–9.
- [13] Al-Dulaijan SU. Sulfate resistance of plain and blended cements exposed to magnesium sulfate solutions. *Constr Build Mater* 2007;21:1792–802.
- [14] Sakr K. Effect of cement type on the corrosion performance of reinforcing steel bars exposed to acidic media using electrochemical techniques. *Cem Concr Res* 2005;35:1820–6.
- [15] Dhir RK, Jones MR, McCarthy MJ. PFA concrete: chloride-induced reinforcement corrosion. *Mag Concr Res* 1994;46:269–77.
- [16] Moreno M, Morris W, Alvarez MG, Duffo GS. Corrosion of reinforcing steel in simulated concrete pore solutions: effect of carbonation and chloride content. *Corros Sci* 2004;46:2681–99.
- [17] Yu H, Chiang KTK, Yang L. Threshold chloride level and characteristics of reinforcement corrosion initiation in simulated concrete pore solutions. *Constr Build Mater* 2012;26:723–9.
- [18] Pradhan B, Bhattacharjee B. Corrosion zones of rebar in chloride contaminated concrete through potentiostatic study in concrete powder solution extracts. *Corros Sci* 2007;49:3935–52.
- [19] Zuquan J, Wei S, Yunsheng Z, Jinyang J, Jianzhong L. Interaction between sulfate and chloride solution attack of concretes with and without fly ash. *Cem Concr Res* 2007;37:1223–32.
- [20] Al-Amoudi OSB, Maslehuddin M, Abdul-Al YAB. Role of chloride ions on expansion and strength reduction in plain and blended cements in sulfate environments. *Constr Build Mater* 1995;9:25–33.
- [21] Al-Amoudi OSB, Maslehuddin M. The effect of chloride and sulfate ions on reinforcement corrosion. *Cem Concr Res* 1993;23:139–46.
- [22] Polder RB. Test methods for onsite measurement of resistivity of concrete – a RILEM TC-154 technical recommendation. *Constr Build Mater* 2001;15:125–31.
- [23] Pradhan B, Bhattacharjee B. Performance evaluation of rebar in chloride contaminated concrete by corrosion rate. *Constr Build Mater* 2009;23:2346–56.
- [24] Alghamdi SA, Shamsad Ahmad. Service life prediction of RC structures based on correlation between electrochemical and gravimetric reinforcement corrosion rates. *Cem Concr Compos* 2014;47:64–8.
- [25] IS 383-1970 (Reaffirmed 2002). Specification for coarse and fine aggregates from natural sources for concrete. New Delhi: Bureau of Indian Standards; 2002.
- [26] Neville AM, Brooks JJ. Concrete technology. Delhi: Pearson Education; 2004.
- [27] Law DW, Millard SG, Bungey JH. Linear polarisation resistance measurements using a potentiostatically controlled guard ring. *NDT & E Int* 2000;33:15–21.
- [28] Gu GP, Beaudoin JJ, Ramachandran VS. Techniques for corrosion investigation in reinforced concrete. In: Ramachandran VS, Beaudoin JJ, editors. Handbook of analytical techniques in concrete science and technology. New Jersey: Noyes Publications; 2001. p. 441–504.
- [29] Erdogdu S, Bremner TW, Kondratova IL. Accelerated testing of plain and epoxy-coated reinforcement in simulated seawater and chloride solutions. *Cem Concr Res* 2001;31:861–7.
- [30] ASTM C876-09. Standard test method for corrosion potentials of uncoated reinforcing steel in concrete. West Conshohocken (PA): ASTM International; 2009.
- [31] Al-Amoudi OSB. Sulfate attack and reinforcement corrosion in plain and blended cements exposed to sulfate environments. *Build Environ* 1998;33:53–61.
- [32] Rasheeduzzafar, Al-Amoudi OSB, Abduljauwad SN, Maslehuddin M. Magnesium–sodium sulfate attack in plain and blended cements. *J Mater Civ Eng ASCE* 1994;6:201–22.
- [33] Hicks CR. Fundamental concepts in the design of experiments. 3rd ed. New York: Holt, Rinehart and Winston; 1982.