INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title: 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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SHORT 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. 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 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. 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. Among different methods, the 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 (C_F), and total chloride ion (C_T) 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: $CaCl_2 > MgCl_2 > NaCl$ 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. 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.

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 $CaCl_2$+$MgSO_4$ solution as compared to NaCl+$MgSO_4$ solution followed by $MgCl_2$+$MgSO_4$ solution. 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 obtained results showed that the free chloride ion (C_F) content at all depth intervals from exposure surface as well as the apparent chloride diffusion coefficient (D_{app}) of OPC and PPC concrete admixed with and without different corrosion inhibitors, and exposed to chloride solutions decreased in the order of $NaCl > CaCl_2 > MgCl_2$, whereas the chloride binding capacity (R) decreased in the order of R: $CaCl_2 > MgCl_2 > NaCl$. In case of exposure to composite chloride-sulfate solutions, the free chloride content decreased in the order of C_F: $CaCl_2+MgSO_4 > NaCl+MgSO_4 > MgCl_2+MgSO_4$, and the chloride diffusion coefficient decreased in the order of D_{app}: $MgCl_2+MgSO_4 > NaCl+MgSO_4 > CaCl_2+MgSO_4$. 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: $NaCl+MgSO_4 > MgCl_2+MgSO_4 > CaCl_2+MgSO_4$ 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 $NaNO_2$. 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 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.