# INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
## SHORT ABSTRACT OF THESIS

Name of the Student : Arya Anuj Jee

Roll Number : 136104012

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Influence of mix parameters, and exposure solution and duration on chloride ingress, microstructure, and steel reinforcement corrosion in concrete exposed to chloride and composite chloride-sulfate environment

Name of Thesis Supervisor(s) : Prof. Bulu Pradhan

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## SHORT ABSTRACT

In reinforced concrete structures, concrete generally provides physical and chemical protection to the steel reinforcement during the service life. The reinforced concrete structures, located in coastal areas, and in the areas where the soil and groundwater are contaminated with chloride and sulfate salts, generally experience durability problems that result in deterioration of concrete. Among the durability problems, corrosion of steel reinforcement is the most serious one that is encountered in reinforced concrete structures around the world. Chloride ions are considered to be the primary cause of reinforcing steel corrosion in concrete. The chloride penetration modelling based on Fick's second law of diffusion is a conventional approach to forecast the rebar corrosion in concrete caused by chloride ingress. The estimated chloride diffusion coefficient can be used for predicting the service life of reinforced concrete structures. In case of exposure to sulfate-bearing soil and ground water, and marine environment, the penetration of sulfate ions into the structures results in sulfate attack. In case of ingress of both chloride and sulfate ions concomitantly (from marine environment, and sulfate-bearing soil and groundwater), the reaction mechanism becomes more complex as a result of simultaneous reaction of both chloride and sulfate ions with the hydrated cement phases of concrete.

The present research work focused on evaluating the influence of mix parameters (i.e. binder type, and w/b ratio), exposure solution, and exposure duration on chloride ingress, chloride binding, microstructure, and corrosion of steel reinforcement in concrete exposed to chloride and composite chloride-sulfate environment. For this purpose, prismatic reinforced concrete specimens of size 62 mm × 62 mm × 300 mm with a centrally embedded reinforcing steel bar were prepared from different types of binder, and w/b ratio, and exposed to chloride and composite chloride-sulfate solutions. The reinforced concrete specimen, and test setup used in the present research work were designed in such a way that all the parameters i.e. half-cell potential ($E_0$), corrosion current density ($I_{corr}$), apparent chloride diffusion coefficient (D), and rebar surface chloride concentration ($C_{rs}$) were determined from the same specimen. After obtaining these parameters, the empirical relationships were developed between corrosion current density ($I_{corr}$), and the parameters such as half-cell potential ($E_0$), apparent chloride diffusion coefficient (D), and rebar surface chloride concentration ($C_{rs}$) of concrete. The concrete mixes were prepared from different types of binder such as ordinary Portland cement (OPC), OPC replaced with

20% fly ash (OPC+ 20% FA), and Portland pozzolana cement (PPC) at w/b ratios of 0.45, 0.50, and 0.55. Tempcore TMT (Thermomechanically treated) steel bar was used as the steel reinforcement. The prismatic specimens were exposed to chloride, and composite chloride-sulfate solutions with alternate wetting-drying cycles till the exposure period of 27 months. Sodium chloride (NaCl) of different concentrations i.e. 1%, 3%, and 5% was used in the preparation of chloride solutions. Similarly, NaCl concentrations of 1%, 3%, and 5%, and magnesium sulfate ($MgSO_4$), and sodium sulfate ($Na_2SO_4$) concentrations of 2%, and 4% each were used in the preparation of composite chloride-sulfate solutions i.e. NaCl with $MgSO_4$, and NaCl with $Na_2SO_4$. Half-cell potential measurement, and corrosion current density by linear polarization resistance (LPR) measurement were carried out on the prismatic specimens at the start of wetting period of wetting-drying cycle at every 3-month interval of exposure till the exposure period of 27 months. At the end of exposure periods i.e. 9, 15, 21, and 27 months, the concrete powder samples were collected by drilling throughout the exposure surface of prismatic specimens at five depth intervals each of 5 mm i.e. 0-5 mm, 5-10 mm, 10-15 mm, 15-20 mm, and 20-25 mm from the exposure surface of concrete up to the level of embedded reinforcing steel bar. The collected concrete powder samples were used for determining the free chloride content, and total chloride content, and for carrying out the microstructure analysis (X-ray diffraction (XRD) analysis, Field emission scanning electron microscope (FESEM) analysis, and Thermo-gravimetry analysis (TGA)) of concrete. After determining the free chloride content over different depth intervals from the exposure surface of concrete, the apparent chloride diffusion coefficient was estimated using Fick's second law of diffusion by keeping in view the convection zone observed in some cases.

The results of free chloride content indicated the presence of convection zone near the exposure surface region of concrete, which was dependent on binder type, w/b ratio, exposure solution, and exposure duration. The presence of sulfate ions reduced the penetration of chloride ions into concrete exposed to composite chloride-sulfate solutions as compared to chloride solutions, and the free chloride content in concrete decreased with increase in concentration of $MgSO_4$ or $Na_2SO_4$ in the composite chloride-sulfate solutions. Further, the free chloride content was lower in the concrete exposed to composite solutions of NaCl + $Na_2SO_4$ as compared to composite solutions of NaCl + $MgSO_4$ at all depth intervals. Among binder type, the free chloride content was higher in PPC concrete at lower depth intervals (i.e. near the exposure surface) as compared to OPC + 20% FA followed by OPC concrete whereas at higher depth intervals the free chloride content was higher in OPC concrete as compared to OPC + 20% FA followed by PPC concrete. Further, the concrete made with PPC exhibited higher resistance against chloride ingress as compared to OPC + 20% FA followed by OPC concrete. The presence of sulfate ions reduced the apparent chloride diffusion coefficient of concrete exposed to composite chloride-sulfate solutions as compared to chloride solutions, and the chloride diffusion coefficient was mostly higher in the concrete exposed to composite solutions of NaCl with $MgSO_4$ as compared to composite solutions of NaCl with $Na_2SO_4$. Among binder type, the concrete made with OPC exhibited higher apparent chloride diffusion coefficient as compared to OPC + 20% FA followed by PPC. In addition, the apparent chloride diffusion coefficient was lower in the concrete made with lower w/b ratio as compared to higher w/b ratio. The presence of sulfate ions in the exposure solution altered the chloride binding in concrete during early, and later exposure periods. Among binder type, the concrete made with OPC exhibited higher chloride binding as compared to that made with OPC + 20% FA followed by PPC at all exposure periods.

The formations of different compounds as indicated by the results of XRD analysis varied with the depth from exposure surface of concrete, type of exposure solution, concentration of chloride and sulfate ions in the exposure solution, cation associated with sulfate ions, binder type, and w/b ratio. The variations in the formation of ettringite, calcium chloroaluminate, and calcium hydroxide, as indicated by the peak intensity and wt. % from XRD analysis, in the concrete exposed to chloride, and composite chloride-sulfate solutions were consistent with the variations in the obtained free chloride content of concrete. The formations of ettringite, calcium chloroaluminate, calcium hydroxide, gypsum, and magnesium hydroxide in the concrete as indicated by the XRD patterns were also confirmed from the obtained FESEM images. As observed from the results of TGA, the total mass loss was mostly higher in OPC concrete as compared to that in OPC + 20% FA, and PPC concrete in case of exposure to chloride and composite chloride-sulfate (for both cations i.e. $Mg^{2+}$ and $Na^{+}$) solutions. Further, the variations in mass loss of concrete due to dehydration of calcium hydroxide, ettringite, calcium chloroaluminate, and gypsum were mostly consistent with the variations in the peak intensity and wt. % of these compounds obtained from XRD analysis.

From the viewpoint of corrosion behaviour of steel reinforcement evaluated through half-cell potential, and corrosion current density, the concrete made with PPC showed better performance than OPC + 20% FA, and OPC concrete against exposure to chloride, and composite chloride-sulfate solutions. Similarly, the concrete made with lower w/b ratio exhibited better corrosion performance than that made with higher w/b ratio against exposure to chloride, and composite chloride-sulfate solutions. The empirical relationships developed between corrosion current density ($I_{corr}$) and the parameters i.e. half-cell potential ($E_0$), apparent chloride diffusion coefficient (D), and rebar surface chloride concentration ($C_{rs}$) for OPC, and PPC concrete exposed to chloride and composite chloride-sulfate solutions predicted the corrosion current density of steel reinforcement for OPC + 20% FA concrete with greater accuracy, which was independent of the empirical model development. Further, the developed empirical relationship between corrosion current density ($I_{corr}$), and half-cell potential ($E_0$) predicted well the corrosion current density ($I_{corr}$) values reported in the literature for chloride exposure conditions.