EFFECT OF CHLORIDE ION, SULFATE ION AND CONJOINT CHLORIDE-SULFATE IONS ON CORROSION BEHAVIOUR OF STEEL REINFORCEMENT AND PERFORMANCE OF CONCRETE

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ABSTRACT

Reinforced concrete structures are affected by various durability problems during their service life. Deterioration due to corrosion of steel reinforcement and degradation of concrete due to sulfate attack are the most significant durability problems encountered in reinforced concrete structures and have major financial implications around the world. Concrete durability problems are the major cause of concern all over the world especially in the coastal areas where the structures are subjected to both chloride induced reinforcement corrosion and sulfate attack, and mechanism of deterioration may become more complex because of ingress of both chloride and sulfate ions. Chloride and sulfate ions can either be present in the concrete ingredients (internal) and/or penetrate into the hardened concrete from outside environment (external). The corrosion behaviour of steel reinforcement and the performance of concrete may vary significantly in the conjoint presence of chloride-sulfate ions as compared to that in the presence of only chloride and sulfate ions. In this research work, a comprehensive experimental investigation has been carried out to study the effect of conjoint presence of chloride ions and sulfate ions along with the associated cation type on corrosion behaviour of steel reinforcement in electrolytic concrete powder solution (ECPS) and in concrete by incorporating different types of cement, steel and water-cement (w/c) ratio. In addition, to analyze the effect of chemical composition of the electrolytic concrete powder solution on corrosion behaviour of steel reinforcement, the ionic concentration, pH and conductivity of the concrete powder solutions were determined. Further, the performance of concrete by incorporating different types of binder and water-binder ratios (w/b ratio) under different exposure conditions in sulfate and conjoint chloride-sulfate environment was assessed. To evaluate the changes in phase composition of hardened concrete in the presence of chloride and sulfate ions, various microstructural techniques such as X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), and Fourier transform infrared (FTIR) spectroscopy analyses were also carried out.

In the present research work, the entire experimental program was divided into three series. In series I, the effect of chloride and conjoint chloride-sulfate contamination on 28 day compressive strength of concrete; microstructural changes occurred in concrete due to the presence of chloride and conjoint chloride-sulfate ions; ionic concentration, pH and conductivity of electrolytic concrete powder solution; and corrosion behaviour of steel in electrolytic concrete powder solution (ECPS) have been investigated. For this purpose, two types of cement namely: ordinary Portland cement (OPC) and Portland pozzolana cement (PPC), and two types of thermo-mechanically treated (TMT) steel bars of diameter 12 mm namely Tempcore TMT and Thermex TMT steel bars were used as the steel reinforcement. The concrete mixes were prepared with two w/c ratios of 0.45 and 0.5. Chloride and sulfate salts were admixed at the time of preparation of concrete in the mixing water as percentage by mass of cement content. Sodium chloride (NaCl) was used as the source of chloride ions, whereas sodium sulfate (Na_2SO_4) and magnesium sulfate ($MgSO_4$) were used as the sources of sulfate ions. The concentrations of NaCl used were 3%, 5% and 7% and those of Na_2SO_4 and $MgSO_4$ used were 3%, 6% and 12% each by mass of cement content. A total of 1056 cube specimens of size 150 mm were prepared from 88 concrete mixes (i.e. from control mix and mixes contaminated with varying concentrations of chloride and composite chloride-sulfate salts) with twelve replicate specimens from each mix. The cube specimens were subjected to moist curing till the age of 28 days from the day of preparation. After that, three replicate specimens from a given concrete mix were tested to determine the 28 day compressive strength and remaining nine replicate specimens were kept in laboratory exposure condition till the period of 56 days for obtaining the concrete powder. From the obtained concrete powder, electrolytic concrete powder solutions (ECPS) was prepared. The obtained electrolytic concrete powder solution was chemically analyzed to determine its ionic concentration, pH and conductivity. The electrochemical tests such as potentiodynamic polarization test and linear polarization resistance (LPR) test on bare steel specimens were conducted in electrolytic concrete powder solution. A total of 704 bare steel specimens were prepared and tested. From the potentiodynamic polarization test on bare steel specimens in ECPS, anodic polarization curves were obtained and these were used to identify different zones of corrosion namely active zone, passive zone and pitting zone. From these zones of corrosion, corrosion potential (E_{corr}), act/pass boundary potential and pass/pitt boundary potential were determined. From LPR test, the variations in corrosion potential and corrosion current density of steel reinforcement in electrolytic concrete powder solution were evaluated. The results of 28 day compressive strength of cube specimens prepared from OPC and PPC concrete admixed with chloride and chloride-sulfate ions at w/c ratios of 0.45 and 0.5 indicated that the varying concentrations of chloride and chloride-sulfate ions have significant effect on compressive strength of concrete. The results of microstructural changes occurred in concrete due to chloride and chloride-sulfate contamination (studied through XRD, FTIR and FESEM analyses) showed the formation of various compounds and also indicated the variations in the formations of these compounds due to the effect of cement type, concentrations of chloride salts and sulfate salts along with the associated cation type. The results obtained from the measurement of ionic concentration, pH, and conductivity of electrolytic concrete powder solution indicated that the change in cement type, w/c ratio, concentrations of admixed NaCl, Na_2SO_4 and $MgSO_4$ and cation type associated with sulfate ions i.e. Na^+ and Mg^{++} affect the electrolytic concrete powder solution chemistry. From the results of potentiodynamic polarization test on bare steel specimens in ECPS, it is found that the presence of sodium sulfate in chloride environment has mitigated the effect of chloride ions on reducing the passivity of both types of steel reinforcement. On the other hand, the presence of magnesium sulfate in chloride environment has stimulated the effect of chloride ions on reducing the passivity of steel reinforcement for Tempcore TMT steel whereas Thermex TMT steel performed better in the conjoint presence of NaCl and $MgSO_4$ in maintaining the passivity as compared to that in the presence of only NaCl. From the effect of cation type i.e. Na^+ and Mg^{++} associated with sulfate ions, it is inferred that the range of passive zone of both Tempcore TMT and Thermex TMT steel is more in NaCl plus Na_2SO_4 environment as compared to that in NaCl plus $MgSO_4$ environment for both types of cement and w/c ratio. This implies that Mg-oriented sulfate attack is more aggressive in the presence of chloride ions in reducing the passivity of steel reinforcement as compared to Na-oriented sulfate attack. From the results of LPR test on bare steel specimens in electrolytic concrete powder solution, it is observed that Tempcore TMT steel, OPC and w/c ratio of 0.5 showed lower corrosion current density in NaCl and NaCl plus $MgSO_4$ environment, thereby likely to exhibit longer corrosion propagation period. Similarly in NaCl plus Na_2SO_4 environment, Tempcore TMT steel, PPC and w/c ratio of 0.5 are likely to exhibit longer corrosion propagation period. Further, there exists a good correlation between passivity range and corrosion parameters (corrosion potential and corrosion current density) of steel reinforcement in NaCl, NaCl plus Na_2SO_4 and NaCl plus $MgSO_4$ contaminated electrolytic concrete powder solutions.

In series II, the corrosion behaviour of steel reinforcement embedded in chloride-sulfate contaminated concrete and subsequently exposed to chloride-sulfate environment was investigated by measuring corrosion potential and corrosion current density at the age of 90, 180 and 270 days from the day of preparation of the specimens by using linear polarization resistance (LPR) technique. For this purpose prismatic reinforced concrete specimens of size 72 mm × 72 mm × 300 mm with a steel bar of 12 mm diameter placed centrally with a concrete cover of 30 mm on all the sides and at the bottom were prepared using ordinary Portland cement (OPC), Portland pozzolana cement (PPC), OPC plus 20% fly ash (OPC+20FA) and OPC plus 30% fly ash (OPC+30FA) at a w/b ratio of 0.5. Tempcore TMT and Thermex TMT steels were used as the steel reinforcement. Chloride and sulfate salts were admixed at the time of preparation of concrete in the mixing water as percentage by mass of binder content. The admixed concentrations of NaCl were 3%, 5% and 7% and those of Na_2SO_4 and $MgSO_4$ were 3% and 6% each. A total of 312 prismatic reinforced concrete specimens were prepared from 52 concrete mixes (i.e. from control mix and mixes contaminated with varying concentrations of composite chloride-sulfate salts) with three replicate specimens from each mix and for each type of steel. After 28 days of moist curing, the prismatic reinforced concrete specimens were removed from the curing tank and were kept in the laboratory exposure condition for a period of 90 days from the day of preparation. After that, the specimens were exposed to normal water and composite chloride-sulfate solutions (concentration of salts in the solution same as that admixed at the time of preparation of concrete specimens) with alternate wetting-drying cycles (each cycle comprising of 7 days of partial immersion in the test solution followed by 14 days of drying in the laboratory condition). From the results it is observed that the probability of occurrence of steel reinforcement corrosion in concrete increased in the presence of chloride and sulfate ions for all types of binder and steel reinforcement. From the variations in corrosion current density, it is observed that the corrosion current density of both types of steel in blended cement concrete specimens were lower than those in OPC concrete specimens in the conjoint presence of NaCl plus Na_2SO_4, whereas the opposite variation was observed in the conjoint presence of NaCl plus $MgSO_4$ i.e. the corrosion current density values in OPC concrete were lower than those in blended cement concrete specimens. Further Tempcore TMT steel exhibited lower corrosion density as compared to Thermex TMT steel in the composite chloride-sulfate environment.

In series III, the effect of sulfate ions and that of composite chloride-sulfate ions on deterioration of concrete have been investigated through the measurement of change in weight and compressive strength of cube specimens after 360 days of exposure to these aggressive ions. Further to examine the effect of sulfate ions and conjoint sulfate-chloride ions on the microstructure of hardened concrete. XRD and FESEM analyses were also conducted. Cube specimens of size 150 mm were prepared with different types of binder such as OPC, PPC and OPC plus fly ash at different replacement levels (20% and 30% by mass of binder content) and w/b ratios of 0.45 and 0.5. A total of 912 cube specimens were prepared from different concrete mixes. The specimens were subjected to moist curing in curing tank till the age of 28 days from the day of preparation and were then kept in the laboratory condition for a period of 7 days. After that, the specimens were exposed to normal water, sulfate solutions and composite chloride-sulfate solutions. The concentrations of NaCl used in the preparation of exposure solutions were 3% and 5% and those of Na_2SO_4 and $MgSO_4$ used were 3%, 6% and 12% each. The exposure solutions were prepared by dissolving the required quantities of Na_2SO_4, $MgSO_4$, NaCl plus Na_2SO_4 and NaCl plus $MgSO_4$ in water. From each concrete mix, three replicate cubes were subjected to a given exposure solution with alternate wetting and drying cycles comprising of 7 days of full immersion in the exposure solution followed by 14 days of drying in the laboratory condition and another set of three replicate cubes were continuously immersed in the exposure solution till the end of exposure period. The results indicated that the effect of sulfate attack in terms of weight loss of concrete was more prominent in sulfate and composite chloride-sulfate exposure solutions when the sulfate ion is associated with Mg^{++} cation as compared to that associated with Na^{+} cation. While comparing the effect of exposure solutions on compressive strength of concrete, it is observed that the reduction in compressive strength of concrete decreased in the order: $MgSO_4 > Na_2SO_4 >$ NaCl plus $MgSO_4 >$ NaCl plus Na_2SO_4. This implies that chloride ions mitigate the sulfate attack on concrete when concomitantly present with sulfate ions.