Prediction of Long Term Diffusion Behaviour of Chloride in Concrete

EXECUTIVE SUMMARY

The long term diffusion behavior of chloride in concrete structures that got exposed to sea water during the Asian Tsunami disaster was studied, as chlorides corrode the steel reinforcement and weaken the structure. A barrier of flyash containing concrete PCC was laid over the exposed surface before building the subsequent structure. It was necessary to ensure the long term safety of the structure. Using a combination of numerical and experimental methods, the chloride distribution profile as a function of depth and time was obtained. Studies showed the chloride content to be well below the allowable limit even for 150 years.

OUTLINE

The entry of seawater into PFBR construction site demanded a study on the extent of chloride ingress in the concrete pours and its consequences on the structure built subsequently. Fig. 1 schematically shows the concrete pours 1 and 2 (P1 and P2) inundated with seawater. Chloride concentrations at different depths in P1 and P2 were evaluated by BHAVINI. Chloride in the newly built layers consisting of 100 mm of PCC(concrete with 30% fly ash) as a diffusion barrier, followed by normal structural concrete (Shg = V), was 0.05 kg/m³, which is well within the permissible limit of 0.6 Kg/m³ (as per IS: 456-2000). However, it was essential to ascertain that an increase, if any, in chloride concentration in the concrete structure due to diffusion from beneath is also within the permissible limit during prolonged service of 150 years.

The chloride ingress from the seawater exposed concrete to the PCC and structural concrete, was modeled based on one-dimensional diffusion mechanism. One-dimensional diffusion equations with appropriate initial concentrations and boundary conditions were solved using Numerical methods. The predicted chloride distributions as a function of distance for 60, 100 and 150 years and as a function of time at a position (PCC barrier) were evaluated. Inputs like initial concentrations and diffusion coefficients of chloride in concrete (Dc) and PCC (DPCC) were obtained from experimental data and reports on similar type concrete. The predicted chloride concentrations were always well below the allowable limit on the surface of the PCC (Fig. 2(a)) and in the entire structure even after 150 years (Fig. 2(b)).

The selection of ‘D’ and its sensitivity on the concentration profiles were validated since ‘D’ values were taken from literature. Concentration profiles as a function of time (up to 150 years) at a distance of 100 mm above P2 were evaluated by an analytical method using D values ranging from 10⁻¹¹ to 10⁻⁷ m/sec, reported for different types, exposure and testing conditions of concrete. It was seen that the concentration always remained below the permissible level of 0.6 Kg/m³, even for a ‘D’ value as high as 10⁻⁷ m/sec. This is far higher than the highest value reported in literature and represents an extreme situation explained below.

Concrete showed an inhomogeneous microstructure consisting of a dispersion of aggregates of different shapes and sizes, binding medium of hydrated cement paste and an interface between cement and aggregates. Chloride was preferentially present in the cement phase. During curing, water reacts with tricalcium silicate to form the porous hardened cement paste, where chloride species predominantly exist within the pores. Chloride in a concrete cured in sea water evaluated using Proton Induced X-ray Emission gave a ‘D’ value of ~1.8 x 10⁻⁸ m²/s. Such a value higher than that reported ~10⁻¹¹ to 10⁻¹⁰ m²/s is due to the undeveloped pore system in the wet concrete in the initial stages of hydration of cement. This diffusion process, although could have proceeded indefinitely is arrested by the simultaneous hydration process of cement, which hardens the concrete introducing an impermeable, tighter pore system. Hence, such high rates of diffusion are not expected in cured concrete, which was also seen from the calculated chloride profile. The concentration is below the allowable limit up to 150 years for value of D as high as 10⁻⁷ m²/sec which is an extreme situation not encountered during service. This study showed that the accidental exposure of the concrete pours to sea water has no adverse effect on the concrete structure above after long years of service.

![Fig. 1: Schematic Elevation view of a section of a concrete built-up](image)

![Fig. 2: Chloride concentration profile in concrete as a function of (a) time at the surface of PCC (b) depth after service life of 150 years.](image)
HARMFUL EFFECT OF CHLORISE ON CONCRETE

Two physico-chemical processes, carbonation and chlorination limit the useful life of reinforced concrete. Normally, the steel bars in reinforced concrete are protected by high alkalinity (pH ~ 13) of the concrete. However, some reactions between species like Ca(OH)₂ and CO₂ reduce the pH. This is called carbonation and is harmful to the formation of passive ferric oxide film around the embedded steel bars. A complete breakdown of the passive film occurs when the ratio of concentration of chloride to hydroxide exceeds 0.6, or when the concentration of chloride ions in the concrete exceeds 0.05 wt %. Chlorides in water trapped at pores in concrete, introduce the same effect. Chlorination of the concrete is also deleterious to its mechanical behavior. Hence, the acceptable level of chloride in concrete is specified to be as low as 0.05 wt %.

MICROSTRUCTURE OF SEAWATER CURED CONCRETE

Concrete exhibits a complex non-homogeneous microstructure, consisting of stone/sand aggregates of various sizes/shapes, hydrated cement paste, interfacial transition zone—corresponding to the interface between the aggregates & hydrated cement paste, and system of voids/microcracks. Cement is primarily a mixture of oxides of various elements like calcium, aluminum, silicon and calcium sulphate. Upon mixing with water, the oxides combine with water, by a hydration reaction forming various hydrated products such as C-S-H (calcium silicate hydrate) gel, ettringite (calcium aluminum trisulphate, aluminum), AFm (calcium aluminum monosulphate) and calcium hydroxide. Figure 3 shows the SE image of the hydrated cement phase in a sea water cured concrete. The various micro-constituents of cement paste have been identified based on the elemental contrast and their morphology: Ettringite exist as long slender needles, Ca(OH)₂ are precipitated as hexagonal plates, while the C-S-H exhibit a fine layered network. Concretes also exhibit an interconnected pore system of various sizes: macropores, capillary pores between hydration products and fine pores within C-S-H gel. These pores can contain trapped water and the dissolved chloride ions can disperse through the concrete through these void structures. Chlorides reduce the alkaline pH environment provided by the Ca(OH)₂, and increases the susceptibility of corrosion of steel reinforcement.

MODELING OF CHLORIDE DIFFUSION IN CONCRETE

The process of chloride ingress from the surface of the concrete into its bulk has been modeled. One-dimensional diffusion equations were set up with appropriate initial concentrations and boundary conditions and solved using Numerical methods. The predicted Chloride distributions as a function of position at 60/100/150 years and as a function of time at a position corresponding to the top of a fly-ash containing concrete layer laid as barrier, were evaluated. The inputs included initial chloride concentrations, diffusion coefficients of chloride in concrete (Dc) and fly ash containing concrete (D_Pc).

ACHIEVEMENT

The entry of seawater into the PFBR construction site on December 26, 2004, during Tsunami, demanded an assessment of extent of chloride ingress into already laid concrete and its consequences on the structure to be built. This study revealed that chloride content in the newly built concrete would be below the allowable limit of 0.6 kg/m² (as per IS: 456-2000), even after 150 years.

PUBLICATIONS ARISING OUT OF THIS STUDY AND RELATED WORK ALONG WITH THE IMPACT FACTOR


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