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DEVELOPING CHLORIDE RESISTING CONCRETE USING PFA

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ABSTRACT

PFA concrete mixes were designed to optimise resistance to chloride ingress. Chloride binding capacity, intrinsic permeability and their concomitant influence on the coefficient of chloride diffusion have been investigated. PFA replacements up to 67% and exposure concentrations of 0.1, 0.5, 1.0 and 5.0 mole/litre were used. Chloride binding capacity was found to increase with increasing PFA replacement up to 50% and to then decline. It increased with chloride exposure concentration as well as water/binder ratio. The coefficient of chloride diffusion of concrete samples was found to be dependent on both the intrinsic permeability of the concrete and the ability of its cement matrix to bind chlorides. © *1997 Elsevier Science Ltd*

Introduction

A major problem concerning the durability of reinforced concrete structures is corrosion of the steel reinforcement promoted by the presence of chloride ions. Chloride ions can be chemically bound by the cement matrix and the amount bound is mainly dependent on the chemical composition of the cement used (1). Cement which is particularly good at binding, and hence immobilising these ions will provide a high resistance to chloride ingress.

Recently work has been carried out at the Concrete Technology Unit, University of Dundee, into developing concrete mixes that are highly resistant to the ingress of chloride ions. This requires that consideration be given to the principal factors controlling chloride ingress. There is a general agreement in the literature that this centres around concrete microstructure and the chloride binding capacity of the binder used (2). Therefore, to develop such concrete, these factors need to be optimised.

In dealing with this, materials known to provide benefits to both of the above characteristics were considered. Secondly, preference was given to materials that are readily available, economic to use and which possess a certain level of user confidence. The most suitable materials identified to satisfy the above requirements were PFA and GGBS. This paper describes the studies undertaken with PFA. The use of GGBS has been considered in a previous publication (3).

PFA has a high capacity to bind chlorides. The main reason for this can be attributed to its high alumina content, and possibly the amorphous nature of this alumina (1), leading to increased formation of Friedel's salt. However, it should be noted that Arya et al (4) ascribed the increase in chloride binding of PFA cement pastes containing chloride ions added at the mixing stage to the substantial increase in the amount of adsorbed chlorides.

The method of mix proportioning was examined, since in addition to chemical refinement of the microstructure (e.g. by pozzolanic reaction products), there was scope for enhancing chloride resistance by physical means through improving particulate packing.

Experimental Details

Concrete mixes used in this study were proportioned using a mix design method which minimises the volume of voids in the concrete (5). All concrete mixes were designed to have a binder content of 300 kg/m^3 and a water/binder ratio of 0.55, with a varying PFA content: 0, 17, 33, 50, and 67%.

Standard 100 mm cubes were used for measuring strength and air permeability and 100 mm $\phi \times$ 300 mm cylinders for chloride diffusion measurements. Chloride diffusion tests were conducted on 25 mm slices taken from these cylinders at an age of 28 days (6), with a chloride solution containing 5 mole/litre sodium chloride saturated with $Ca(OH)_2$ and maintained at a temperature of 20°C. Air permeability tests, detailed in a previous publication (7), were conducted on cylindrical specimens of 55 mm $\phi \times$ 50 mm, cored from 100 mm cubes. The test was carried out at ages of 28 and 90 days.

Chloride binding capacity was measured on PC and PC/PFA paste samples representing the binder matrix of the concrete mixes. PFA replacement levels of 0, 17, 33, 50 and 67% were used for studying the influence of PFA content on the resulting chloride binding capacity. Pastes with a water/binder ratio of 0.55 were prepared for all replacement levels. For a replacement level of 50%, pastes were also prepared with w/b ratios of 0.44 and 0.66. The test method is detailed in previous publications (3,8), but a brief description of the test is given below.

During the preparation of the test specimen, carbonation and overheating were avoided. After curing the paste specimens for 6 weeks in saturated lime water at a temperature of 20°C, the crust of the 70 mm cubes was removed and the cores crushed and wet sieved to provide samples with a particle size distribution between 0.2 and 2 mm. The samples were vacuum dried in a desiccator with silica gel for 3 days to remove most of the water. They were then stored for 7 days in a desiccator with silica gel and soda lime at 11% RH. Twenty five grams of the specimen was put in a glass beaker and vacuum dried for 2 hours, before the beaker was filled with 30 ml of sodium chloride solution saturated with $Ca(OH)_2$. Sodium chloride solutions with chloride concentrations of 0.1, 0.5, 1.0 and 5.0 mole/litre were used. The beakers were sealed and stored at room temperature for two weeks to reach adsorption equilibrium (8). The solution was pippetted and its chloride concentration measured using an XRF technique detailed in a previous work (9). Chloride binding capacity was calculated using the equation proposed by Tang and Nilsson (8).

Before measuring chloride binding capacity, small specimens were taken from each sample for the determination of $Ca(OH)_2$ content, using thermogravimetry (TG). The weight loss observed at around 450°C due to the loss of water of crystallisation from the calcium hydroxide present, enabled the determination of the content of this compound.

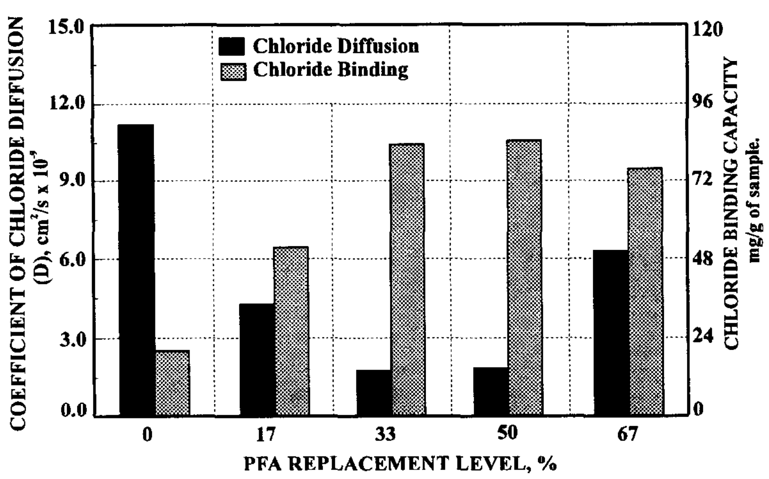

FIG. 1.

Effect of PFA content on chloride diffusion coefficient and chloride binding capacity.

Results and Discussion

Chloride Diffusion

As shown in Figure 1, the coefficient of chloride diffusion (D) decreased sharply with increasing PFA replacement up to 50%. Beyond this level any increase in replacement level led to an increase in the value of D.

Chloride Binding Capacity

Effect of PFA replacement. Figure 1 also shows that as the PFA content increases the chloride binding capacity increases up to a level of 50%. At 50% PFA content and a chloride exposure concentration of 5 mole/litre, the chloride binding capacity increases by a factor of 4 compared with the control. Beyond this level, binding capacity begins to decline with increasing PFA replacement. This may be attributed to the instability of Friedel's salts and its ferrite analogue at low pore solution pH, or as in this case, the chloride solution the samples were exposed to (10,11). The increased solubility and decomposition of these compounds would release chloride ions into the pore solution, raising their concentration level (10). Although the pH values of the chloride solutions were not measured in this research, the results given in Figure 2 show that the $Ca(OH)_2$ content, which makes a major contribution to the alkalinity of the pore solution (12), is greatly reduced with increasing PFA content. Thus, it would appear that up to 50% PFA levels, the reduction in the $Ca(OH)_2$ content is not reduced to a level that threatens the stability of Friedel's salt and its ferrite analogue, but beyond this level it does.

Effect of chloride exposure concentration. The relationship between the chloride exposure concentration and the chloride binding capacity for different PFA contents is shown in Figure 3. Chloride binding capacity increases with chloride concentration for all PFA levels, in a

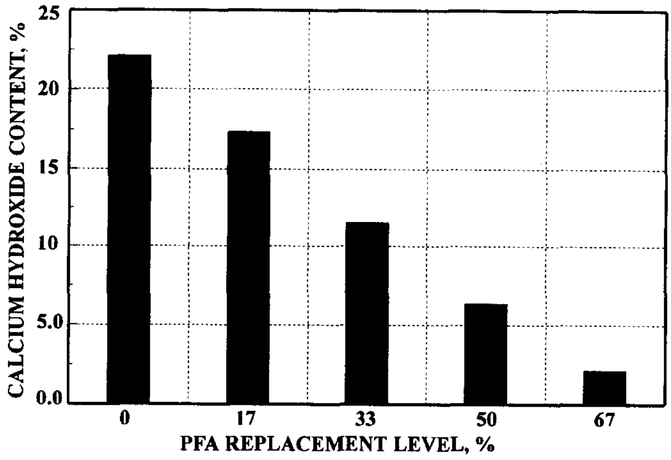

FIG. 2.
Relationship between calcium hydroxide content and PFA replacement level.

directly proportional manner. This may be attributed to the sensitivity of the chloride binding capacity to the ratio of Cl^-/OH^- ions in the solution (13). Chloride binding capacity has been found to increase with increasing Cl^-/OH^- ratio (10). However, Mangat and Molloy (14) have related this increase in the chloride binding capacity to the increased rate of chemical reaction resulting from the higher concentration of the reactants.

Effect of water/binder ratio. Table 1 summarise the effect of w/b ratio on the chloride binding capacities of PC and PFA cement pastes. Some increase in the chloride binding

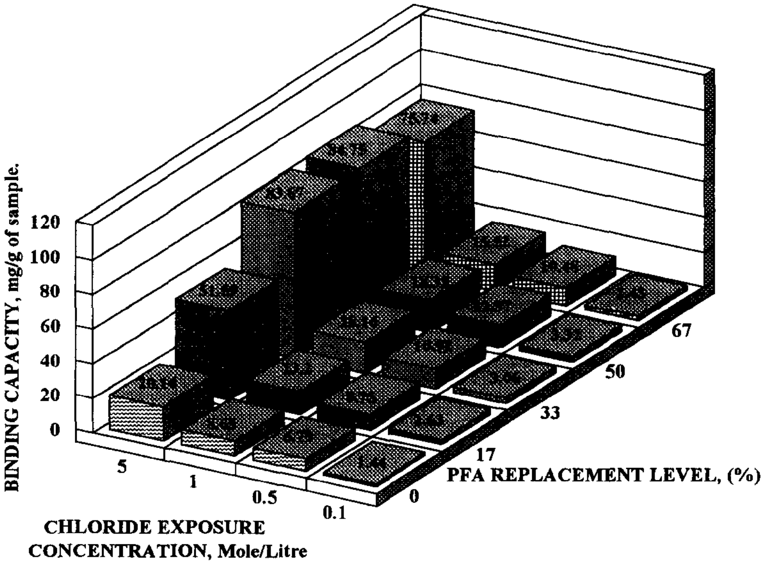

FIG. 3.
Effect of chloride exposure concentration on chloride binding capacity.

TABLE 1
Effect of water/binder ratio on chloride binding capacity of PC and PFA pastes

PFA LEVEL (%)	W/BINDER RATIO	CHLORIDE BINDING CAPACITY, mg/g of sample			
		Chloride Exposure Concentration, Mole/Litre			
		0.10	0.50	1.0	5.0
0	0.66	1.52	7.37	9.63	21.66
0	0.55	1.44	6.79	8.63	20.14
0	0.44	1.41	6.47	8.04	19.29
50	0.55	3.32	12.37	18.05	84.75
50	0.41	3.02	11.94	17.07	83.19
50	0.28	2.79	11.67	16.87	81.91

capacity of both PC and PFA cement pastes is observed with increasing w/b ratio. A similar trend was observed by Tang and Nilsson (8) for PC paste using a similar technique, and by Mangat and Molloy (14) for PFA and GGBS concretes, using pore solution extraction.

Intrinsic Permeability

Figure 4 shows the values of 28 and 90 day intrinsic permeability of PFA concrete at different levels of replacement. At 28 days, with increasing PFA level, permeability decreases up to 33%. Beyond this, permeability starts to increase with increasing PFA level. These results are possibly due to the lower levels of cement, in addition to the relatively low degree of pozzolanic reaction likely to have occurred at this age (15) and, in relation to this, the low quantities of free lime liberated to take part in these reactions. This possible explanation is

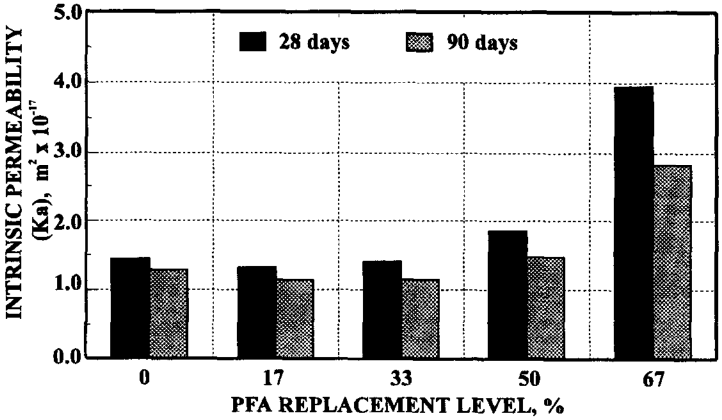

FIG. 4.
Effect of PFA content on the intrinsic permeability of concrete.

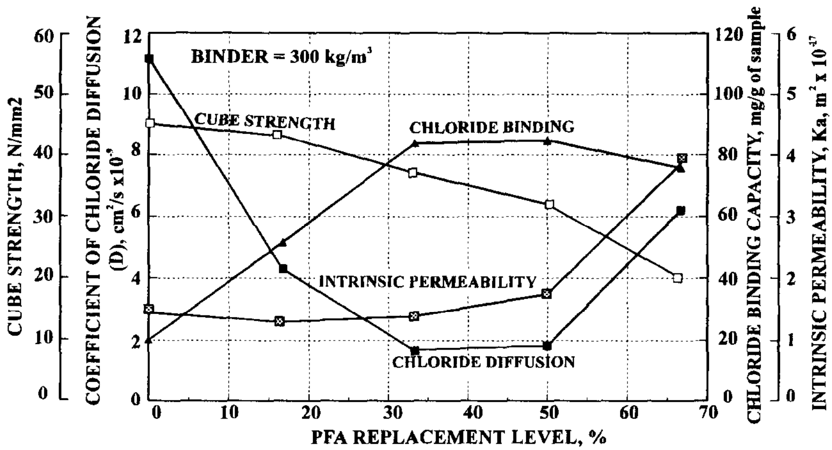

FIG. 5.

Effect of PFA content on intrinsic permeability, chloride binding capacity, cube strength and chloride diffusion coefficient for a varying PFA contents.

reinforced by the results at 90 days, where the rate of improvement in the permeability of PFA concrete is higher than that of the control.

Figure 5 is a plot of strength and intrinsic permeability of PFA concrete, together with the chloride binding capacity and coefficient of chloride diffusion. Up to a PFA level of 33%, intrinsic permeability slightly decreases with increasing PFA level regardless of the lower strength values. Chloride binding capacity increases by a factor of 4 compared to the PC control and the coefficient of chloride diffusion decreases by a factor of 7. The variation in permeation properties is small, suggesting that within this replacement level chloride binding capacity is the determining factor in improving resistance to chloride ingress. The results obtained for concrete with PFA contents between 33 and 50% indicate changes in behaviour compared to that at lower levels of replacement. Over this range a slight increase in intrinsic permeability and the lack of improvement in chloride binding would appear to both contribute in some way to the decrease in resistance to chloride attack.

Conclusions

- Both concrete intrinsic permeability and the ability of the binder matrix to immobilise chloride ions play a role in how resistant concrete is to chloride diffusion.
- PFA pastes offered high chloride binding capacity compared to the PC control. The difference increased with increasing PFA content up to 50%. Beyond this level, chloride binding declined with increasing PFA content, possibly due to the instability of chemically bound chlorides at lower pH levels.
- Chloride binding capacity increased with chloride exposure concentration and also with increasing w/b ratio.
- Up to a 33% PFA level, chloride binding capacity was the dominant factor in improving resistance to chloride attack. However, beyond this range the decline in chloride binding capacity and possibly a slight increase in intrinsic permeability lead to a reduction in concrete resistance to chloride attack.

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