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CONCRETE CONTAINING TERNARY BLENDED BINDERS: RESISTANCE TO CHLORIDE INGRESS AND CARBONATION

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ABSTRACT

This study examined the chloride and carbonation durability performance of concrete containing ternary blended binders in comparison to PC and binary PC/PFA concrete of equivalent standard 28 day cube strengths of 20, 40 and 60 N/mm^2. In addition, the nature of the near surface pore structure of the concrete has been inferred from its initial surface absorption. It has been shown that the chloride resistance of all the ternary binder concrete (TBC) is significantly higher than corresponding PC and PC/PFA mixes. On the other hand, however, under worst case conditions it was found that after 30 weeks accelerated exposure, carbonation depths were generally greater in the TBC mixes. The degree to which this occurred was found to relate to the amount of PC replaced. *© 1997 Elsevier Science Ltd*

Introduction

Many reinforced concrete structures have suffered from premature chloride and/or carbonation induced corrosion damage (1) and the specification of concrete to prevent this has proven to be difficult (2). Benefits, in terms of improved resistance to chloride ingress, through the use of additional materials in binary blends, such as pulverized-fuel ash (PFA), granulated blast furnace slag (GBS) and silica fume (SF), are now well established (3-5). For most practising engineers the concept of using multiple binder combinations, while still rarely used in many countries, is now an option which can be seriously considered for conventional structural concrete. Indeed, examples of major infrastructure projects that have used ternary binder concrete (TBC) include the Stoerbelt bridge/tunnel in Denmark (6) and the Chek Lap Kok bridge, linking to the new Hong Kong airport (7). As limited data on the performance of TBC exists, however, there has been some understandable caution in adopting this technology to date. Against this background, this project has been undertaken to explore the durability performance of TBC and specifically considered was its resistance to chloride and carbonation attack. Selective combinations with PC of common additional binder materials, viz low lime, siliceous PFA to BS EN 450 (1995), GBS to BS 6699 (1991) and SF were used.

TABLE 1

Summary of Concrete Mix Proportions

MIX CODE	28-DAY CUBE STRENGTH, N/mm²	CONSTITUENT MATERIALS, kg/m³					PC/PFA/GBS, PC/PFA or GBS/SF, % by weight
		Binder				Fine Aggregate	
		PC	PFA	GBS	SF		
Series 1(a) - PC control mixes							
M1	20	225	-	-	-	820	100/0/0
M2	40	325	-	-	-	745	100/0/0
M3	60	430	-	-	-	630	100/0/0
Series 1(b) - PC / PFA control mixes							
M4	20	220	95	-	-	600	70/30/0
M5	40	270	115	-	-	540	70/30/0
M6	60	405	175	-	-	360	70/30/0
Series 2(a) - PC / PFA / GBS mixes							
M7	20	140	50	140	-	595	42.5/15/42.5
M8	20	100	120	100	-	565	32.5/35/32.5
M9	20	195	70	195	-	475	25/15/60
M10	20	85	150	195	-	475	20/35/45
M11	40	230	55	100	-	545	60/15/25
M12	40	155	175	155	-	425	32.5/35/32.5
M13	40	155	90	370	-	330	25/15/60
Series 2(b) - PC / PFA / SF mixes ⁺							
M14	20	180	20	-	20	725	80/10/10
M15	20	140	140	-	30	580	45/45/10
M16	40	250	30	-	30	615	80/10/10
M17	40	220	220	-	45	410	45/45/10
M18	60	265	265	-	65	355	45/45/10
Series 2(c) - PC / GBS / SF mixes ⁺							
M19	40	195	-	85	25	625	65/25/10
M20	40	155	-	155	35	580	45/45/10
M21	40	105	-	245	35	545	25/65/10
M22	60	160	-	370	50	370	25/65/10

Note: Free water and natural gravel aggregate contents of 185 and 1,200 kg/m³ respectively were used.
⁺ Nominally 75mm slump achieved with plasticising chemical admixture.

Selection of Binder Materials and Experimental Mix Proportions

TBC mix proportions to give equal 28 day standard cube strengths of 20, 40 and 60N/mm² were established using a mix design method developed at the University of Dundee (8). The binder combinations chosen reflect those typically used in binary mixes and were additionally selected due to their potential to provide a high level of chloride resistance (3-5). The control mixes were PC and PC/30% PFA concrete of equal cube strength. The effect of the binders used was highlighted by maintaining fixed free water and coarse aggregate contents (185 l/m³ and 1200 kg/m³ respectively). A 75 mm nominal slump was obtained without the need for a plasticising chemical admixture except for the SF mixes, where the very cohesive nature required the use of small dosages of superplasticiser. It should be noted that with the free water content selected,

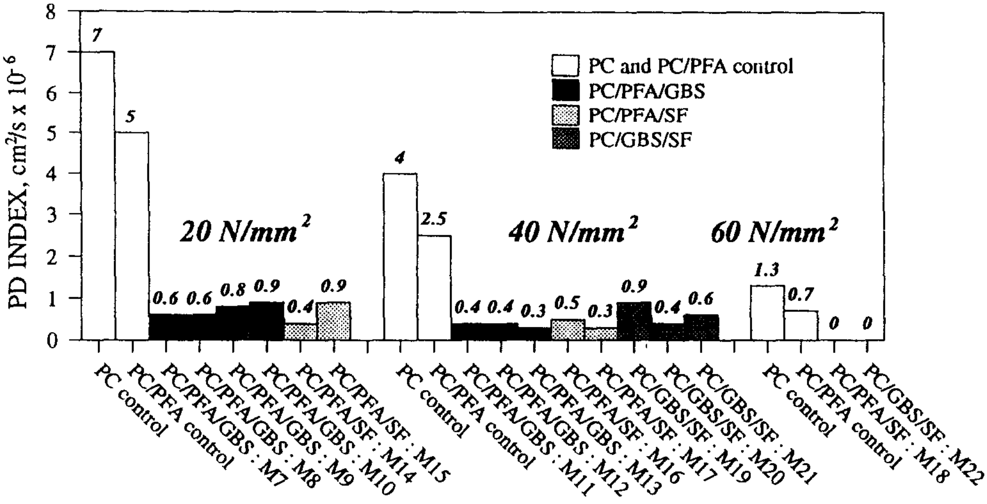


FIG. 1.
Comparison of PD indices obtained for control and TBC mixes.

28 day strengths of 60 N/mm² were not achieved by the PC/PFA/GBS mixes. Unit volumes of the mixes were achieved by varying the fine aggregate contents. A summary of the mix proportions is given in Table 1. It should be noted, that all specimens cast were standard water cured for 28 days prior to their testing, and that all tests reported in this paper were initiated at the age of 28 days.

Electrochemical Chloride Ingress

Given the likely high resistance of the TBC mixes to chloride ingress, an accelerated electrochemical chloride transmission test (9) using 12V DC potential difference (PD) was adopted. PD indices were calculated using Fick's First Law and these are compared for all mixes in Figure 1.

The significant advantage of using TBC mixes is clearly apparent, with the degree of improvement in chloride resistance decreasing slightly with increasing concrete strength.

Considering the 20 N/mm² mixes, PD indices obtained for the TBC were on average 90% and 85% lower than those obtained for the control PC and PC/PFA concrete respectively. Corresponding reductions for 40 N/mm² concretes were on average 89% and 82%. Indeed, no chloride transmission was measured for either of the 60 N/mm² TBC mixes by the conclusion of the 14 day test period.

Most likely reflecting equally very high levels of chloride resistance, there were only minor differences between the PD indices (0.30 minimum to 0.90 maximum) for all the TBC mixes, irrespective of the binder combination used. These variations are, in fact, within the accuracy of the test method and may, therefore, not be significant (9). As the level of PC replacement ranged from between 20 to 80% by weight, the results suggest that no optimum PC replacement existed to achieve maximum chloride resistance.

Accelerated Chloride Penetration

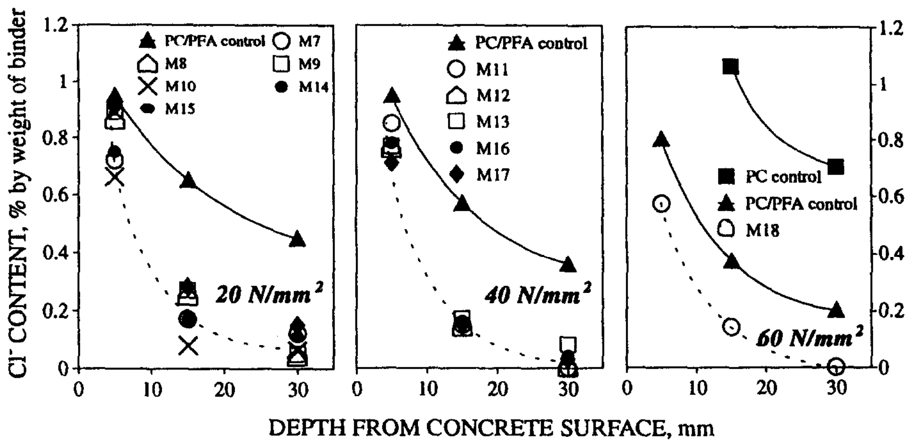
Given the possibility of limited chloride binding due to the rapid nature of the PD test (10), a restricted series of chloride immersion tests in a 5M NaCl solution were carried out (mixes M19 to M22 omitted). Test specimens (75 × 75 × 300 mm prisms) were sealed on 5 faces to give uniaxial penetration. Powder samples were obtained by incremental drilling at 0-5 mm, 6-15 mm and 16-30 mm from the as-cast surface after 28, 56 and 91 days of immersion and the total chloride content determined by XRF analysis.

Chloride profiles are plotted in Figure 2(a), which again shows high levels of chloride resistance for TBC. For example, the TBC mixes had on average 80% lower chloride concentration at 16-30 mm than the PC/PFA control concrete over the range of design strengths. Coefficients of chloride diffusion, calculated using Fick's Second Law, are given in Figure 2(b) which further illustrates the greatly increased performance of the TBC mixes. As was the case in the electrochemical chloride ingress test, these results suggest that similar chloride resistance was obtained for all TBC, regardless of its 28 day strength or binder combination. Indeed, no particular TBC mix again stood out as being optimum.

Accelerated Carbonation

Accelerated carbonation in a partial pressure of 4% CO_2 at 20°C and 50% RH (11) was carried out over 30 weeks or until a carbonation depth of 35 mm was reached. The test specimens were 100 mm cubes, sealed on 5 sides to allow uniaxial carbonation through the as-cast face. The depth of carbonation was measured with phenolphthalein indicator as the mean of 5 points and

(a)



(b)

28 DAY STRENGTH	CHLORIDE DIFFUSION, D ($cm^2 \times 10^{-9}$)													
	PC	PC/PFA	M7	M8	M9	M10	M11	M12	M13	M14	M15	M16	M17	M18
20 N/mm²	45	15	2	1	1	1.7	~	~	~	2.1	3	~	~	~
40 N/mm²	20	8	~	~	~	~	0.5	1	1.1	~	~	0.5	0.4	~
60 N/mm²	7	2.5	~	~	~	~	~	~	~	~	~	~	~	0.4

FIG. 2.

(a) Chloride penetration of control and TBC mixes at 91 days and (b) calculated D values. (Selective PC results were in excess of 1.2% by weight of binder and omitted from figure).

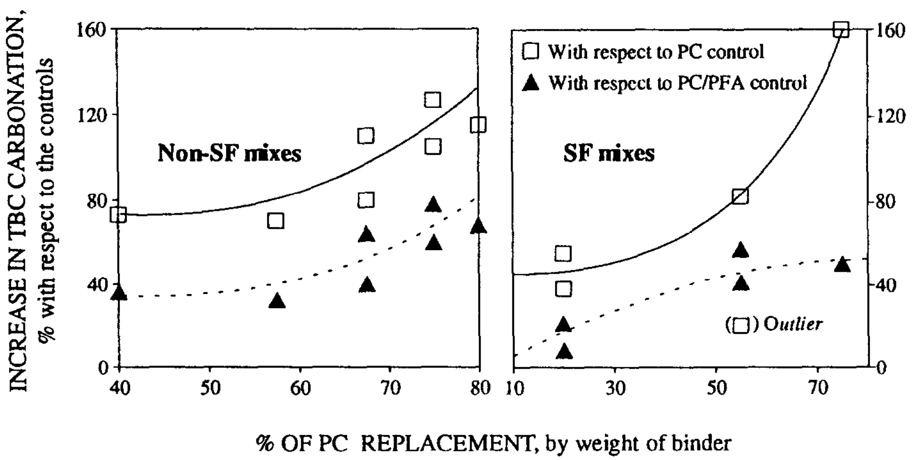


FIG. 3.
Carbonation depths of TBC in comparison to PC and PC/PFA controls.

the results obtained are plotted in Figure 3, in comparison to the equivalent PC and PC/PFA mixes.

The results indicate that, in general, the TBC mixes had significantly higher rates of carbonation than the controls, with carbonation resistance decreasing as the percentage of PC replacement increased. A carbonation depth of 35 mm was reached between 12 to 28 weeks for all 20 N/mm^2 TBC mixes and between 12 to 28 weeks for the 40 N/mm^2 TBC mixes. The exceptions were 40 N/mm^2 mixes M14 and M17, which had carbonation depths at 30 weeks 80% and 88% higher than the PC control (18 mm) and 30% and 35% higher than the PC/PFA control (24 mm) respectively. For the 60 N/mm^2 mixes M16 and M20, corresponding increases were 170% and 215% with respect to the PC control (8 mm) and 80% and 150% with respect to the PC/PFA control (15 mm) at 30 weeks respectively.

Discussion

The relative performance of TBC in comparison to the controls is shown in Table 2. Whilst the improved chloride resistance is clear, there does appear to be a potential problem if such concrete was exposed to a cyclically carbonating environment. Indeed, the results suggest that TBC should not be used in such exposures unless additional protection against carbonation is specified. However, in most chloride-bearing environments the degree of carbonation even for seasonally exposed structures, such as highway infrastructure, is likely to be limited, although local microclimate must be taken into account.

The significant improvements in chloride resistance obtained for TBC mixes may be attributed to either physical and/or chemical influences. Physically, the pozzolanic reactions associated with the use of additional materials is likely to result in improvements to the microstructure of concrete (12). This is supported by initial surface absorption 10 minute test (ISAT-10) results, which indicated a large reduction in surface absorption of the TBC mixes in comparison to the controls. ISAT-10 values of 75.0, 55.0 and 40.0 ml/m^2/sec × 10^{-2} were

TABLE 2

Summary of TBC Durability Performance, with Respect to the Controls

TBC TYPE	PERFORMANCE OF TBC, relative to PC and (PC/PFA) control		
	Chloride Diffusion		Carbonation [++]
	Estimated from PD test [9]	Calculated from penetration test [+]	
Non SF mixes	13.0 (8.0) x better	6.0 (7.5) x better	2.5 (1.5) x worse
SF mixes	15.0 (8.0) x better	8.0 (6.5) x better	2.5 (1.5) x worse

Calculated from; [+] penetration test using Fick's Second Law [10] and [++] Figure 3

obtained for the 20, 40 and 60 N/mm^2 PC concretes respectively, with reductions of 14%, 18% and 50% noted for the corresponding PC/PFA mixes. In contrast, average reductions in ISAT-10 values for the TBC mixes were 63%, 67% and 80% at each strength grade respectively. This trend essentially mirrors that obtained for chloride resistance (Figure 1).

In terms of chemical effects, it has been reported (10) that some aluminate phases in concrete may bind with chloride ions. Although the bulk Al_2O_3 content may be a relatively poor estimate of the actual amount of chloride binding sites, it is at least indicative. Despite variations in total binder content existing between mixes, calculations indicated that the quantity of Al_2O_3 (per kg/m^3) in the majority of TBC mixes was not significantly different than that in the PC/30% PFA control and indeed in many cases was lower, in particular for the SF mixes. This suggests that overall, it is probably the improvement in microstructure that has the dominant effect on the increased chloride resistance of the TBC mixes.

As no obvious optimum mix proportions in terms of chloride resistance were determined from these tests, then optimum replacement levels noted for strength development may be selected. For non-SF mixes and SF mixes this was around 60% and 50% by weight respectively (8). This essentially agrees with the PC replacement levels that gave the lowest carbonation rates as shown in Figure 3.

Conclusions

1. The results obtained from the penetration and electrochemical chloride ingress tests indicated that the chloride resistance of TBC was significantly higher than both PC and PC/PFA control mixes. For 20 and 40 N/mm^2 concrete, PD indices for the TBC were on average 90% and 84% lower than those for the PC and PC/PFA concrete respectively. Furthermore, no chloride transmission was noted with the 60 N/mm^2 TBC mixes by the conclusion of the test.
2. TBC exhibited significantly higher rates of accelerated carbonation than both the PC and PC/PFA concrete controls. Carbonation depths obtained for the TBC mixes were on average 2.5 times higher than those of the PC/PFA control. Carbonation rates for TBC increased with an increased PC replacement level.
3. The initial surface absorption of TBC was significantly reduced in comparison to the controls which, when considered alongside only minor differences in bulk Al_2O_3 content, suggested that the chloride resistance of TBC is, in the main, a result of microstructural refinement.
4. No optimum replacement levels for PC or combinations of binder materials for chloride resistance were found and it is recommended, therefore, that mix proportions are chosen

appropriately to minimise carbonation (i.e. by reducing PC replacement) and/or maximise strength development (i.e. by chosing the optimum replacement levels recommended (8)).

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