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Cement & Concrete Composites 26 (2004) 5–20

Cement & Concrete Composites

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Performance of pfa concrete in a marine environment—10-year results

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Received 15 July 2001; accepted 4 October 2002

Abstract

Steel reinforced 100 × 100 × 300 mm concrete prisms, with nominal strength grades C25, C35 and C45 and different pfa levels (0–50%), were exposed to various curing treatments during the first 28 days prior to exposure in the tidal zone of the BRE marine exposure site. Chloride concentration profiles and rebar weight losses had previously been measured on specimens exposed for 1, 2 and 4 years and this paper reports the results of similar measurements after 10 years exposure. Chloride profiles were also measured for specimens after 1 and 28 days immersion in seawater under laboratory conditions.

Pfa concretes showed substantially increased resistance to the penetration of chlorides compared with control Portland cement (PC) concrete specimens. The improved resistance of the pfa concrete to the penetration of chlorides resulted in reduced corrosion of steel bars imbedded in the concrete. Threshold chloride levels for corrosion, estimated from relationships between steel weight loss and chloride content at the location of the steel, were found to decrease with increasing pfa content. Chloride concentration profiles after 28 days of immersion in seawater showed that considerable chloride penetration occurred during this period due to sorption (capillary suction) of the seawater into the unsaturated specimens. This results in a significant error in diffusion coefficients calculated from the concentration profile using the standard solution to Fick's second law. The error may be substantial for pfa concretes where chlorides penetrating due to sorption immediately after exposure may outweigh subsequent diffusion during continued seawater exposure.

The performance of the concretes, particularly the PC concretes, in this programme is considered in the light of current and new British Standard recommendations for concrete exposed to marine tidal conditions. The adequacy of these recommendations is, however, difficult to assess because the highest concrete quality tested fell a little short of the minimum quality required in the recommendations and cover to reinforcement was also less than required. Nevertheless, the superior performance of concretes containing 30% or more pfa was clearly demonstrated.

Keywords: Chloride diffusion; Chloride threshold; Concrete; Corrosion; Diffusion; Pfa; Marine exposure; Steel reinforcement

1. Introduction

In 1986 a major research programme on the durability of concrete containing pulverized-fuel ash (pfa) was initiated at the Building Research Establishment (BRE) in collaboration with the former Central Electricity Generating Board and Imperial College, London [1]. A principal component of this study was concerned with the effect of pfa on the marine performance of reinforced concrete and, in particular, chloride penetration and protection of reinforcement. Between 1987 and 1989 nearly 1000 concrete specimens, consisting of 100 × 100 × 300 mm reinforced prisms and 100 mm cubes, were cast and placed in the tidal zone of the BRE marine exposure site on the Thames Estuary near Shoeburyness in Essex. Variables studied included strength grade, pfa content and curing history prior to exposure. Specimens have been retrieved at various intervals for the determination of compressive strength, chloride penetration and reinforcing steel corrosion.

Data collected at 1, 2 and 4 years have been reported in previous publications [2–6]; this paper presents some of the test results after 10 years of marine exposure.

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0958-9465/$ - see front matter © 2002 Published by Elsevier Ltd.
doi:10.1016/S0958-9465(02)00117-8

2. Experimental details

2.1. Materials

One Portland cement (PC) conforming to the relevant edition of BS 12 [7] and three different pfas were used in this study. All three of the ashes complied with the chemical requirements of the British Standard for pfa for use as a cementitious component in structural concrete, BS 3892:Part 1:1982 [8] that was in force at the time of commencing this work (as well as with the equivalent requirements in the current, 1997, version of this standard). In addition, two of the three ashes complied with the limit of 12.5% maximum residue on a 45 μm sieve, whilst the third ash had a 45 μm sieve residue of 19.5%. The three ashes would also have met the chemical and physical requirements of ASTM C 618 for Class F fly ash. Chemical analyses of the cement and pfas are given in Table 1.

Table 1
Analysis of cement and pfas (% by mass)

Oxide	PC	Pfa		
		P1	P2	P3
SiO_2	20.55	48.2	48.1	52.4
Al_2O_3	5.07	26.7	24.0	26.0
Fe_2O_3	3.10	11.6	10.6	9.4
CaO	64.51	1.71	6.12	1.69
MgO	1.53	1.62	1.61	1.54
K_2O	0.73	3.18	1.83	2.87
Na_2O	0.15	0.65	0.79	1.32
SO_3	2.53	0.83	0.90	0.85
LOI	1.58	4.34	4.49	2.80
<45 μm	–	11.3	19.5	5.53
Potential compounds (by Bogue method)				
C_3S	57			
C_2S	16			
C_3A	8			
C_4AF	9			

Three series of concrete mixes, of nominal strength grades C25, C35 and C45 (designated G, A and H respectively), and with slump values in the range 30–60 mm, were proportioned using a range of pfa levels (0–50% by mass). A further five series, all of grade C35 and designated B–F, were also made in order to explore the effects of curing on durability (see 'Specimen Curing and Treatment' below for details of curing regimes). In order to achieve strength parity (cube strength after 28 days in water at 20 °C) at a particular strength grade, a cementing efficiency factor, $k = 0.3$, was used for the mix proportioning purposes [9] such that the ratio free water/'effective' cementitious material, $W/(C + kP)$, remained constant within a given series. Advantage was taken of the improved rheological properties of pfa concrete and the mix water was reduced with increasing ash content (approximately 3% water for each 10% ash), but no admixtures were used. Details of mix proportions are given in Table 2.

2.2. Specimen curing and treatment

Concrete specimens from the main G, A and H series were cured at 20 °C for 24 h in their moulds after casting. After demoulding, specimens were either provided with no further curing or stored for a further 2 or 6 days under damp hessian and polythene at 20 °C; this resulted in specimens with a total moist-curing period of

Table 2
Details of concrete mixes

Nominal strength grade	Mix no.	Pfa content (%)	Cement $(C + P)$ (kg/m^3)	$W/(C + P)$	Slump (mm)	28 days strength[a] (MPa)
C25	G1	–	250	0.68	60	32.5
	G2	15% P1	266	0.61	55	33.0
	G3	30% P1	289	0.54	30	34.5
	G4	50% P1	324	0.44	40	33.0
	G5	30% P2	289	0.54	35	33.5
	G6	30% P3	289	0.54	55	33.5
C35	A1	–	300	0.57	50	41.5
	A2	15% P1	319	0.51	45	44.5
	A3	30% P1	346	0.45	40	45.5
	A4	50% P1	392	0.37	30	41.5
	A5	30% P2	346	0.45	50	49.5
	A6	30% P3	346	0.45	50	47.0
C45	H1	–	350	0.49	40	50.0
	H2	15% P1	369	0.44	35	50.0
	H3	30% P1	400	0.39	50	53.0
	H4	50% P1	452	0.32	30	48.0
	H5	30% P2	400	0.39	35	50.5
	H6	30% P3	400	0.39	35	50.5

[a] Mean of results from at least three 100 mm cubes. To convert to approximate cylinder strengths (150 × 300 mm) multiply by 0.8.

1, 3 or 7 days. After moist curing, the specimens were stored at 20 °C and 65% relative humidity until they reached an age of 28 days. The additional series of grade C35 concretes were cured at either 5 or 20 °C for the first 24 h, followed by a further 0, 2 or 6 days moist curing at the same temperature, then stored after moist curing until 28 days in one of the following air-storage conditions (at the same temperature as that used for curing):

Mix series	Temperature (°C)	Relative humidity (%)
E	5	65
F	5	80
B	20	40
A, G, H	20	65
C	20	80
D	20	90

At 28 days concrete specimens were placed in the tidal zone of the BRE marine exposure site on the Thames Estuary at Shoeburyness. The average annual temperature of the seawater at this site is 10 °C and its composition is compared with typical Atlantic Ocean seawater [10] in Table 3.

2.3. Concrete testing

Compressive strength tests were carried out on 100 mm cube specimens after 1, 2 and 10 years exposure; the results upto 2 years have been reported and discussed previously [1,3]. Chloride penetration and steel corrosion data were obtained after various periods of exposure up to 10 years using $100 \times 100 \times 300$ mm reinforced concrete prisms with four pre-weighed, 10 mm diameter, steel bars at 10 or 20 mm nominal cover (two at each cover depth). Fig. 1 shows details of the specimens and testing. Chloride profiles were also measured for specimens after 1 and 28 days immersion in seawater under laboratory conditions.

Powder samples were taken by drilling (in 5 mm depth increments) in eight locations on the four side faces of the prism; the samples were combined to provide a representative sample of each depth increment. Powder samples were ground and analysed by X-ray fluorescence for chloride and calcium. The cementitious content of the sample was calculated using the known calcium oxide content of the cement and pfa, assuming the Thames Valley gravel aggregates to be non-calcareous, and the chloride then expressed as a percentage of the cementitious content. After drilling, the reinforcing bars were removed from the prisms, cleaned manually to remove adhering concrete, soaked in a solution of 50% HCl (containing 0.1% hexamine to inhibit digestion of the steel) to remove all traces of corrosion product, and finally dried and weighed to determine the weight loss due to corrosion. Unexposed samples were also tested in a similar manner to determine background chloride contents and 'processing' weight losses due to cleaning of reinforcing bars.

Table 3
Chemical analysis of seawater

Ions analyzed	Composition (g/l)	
	BRE	Atlantic
Cl^-	18.2	17.8
SO_4^{2-}	2.60	2.54
Ca^{2+}	0.40	0.41
Mg^{2+}	1.20	1.50
Na^+	9.74	9.95
K^+	0.40	0.33

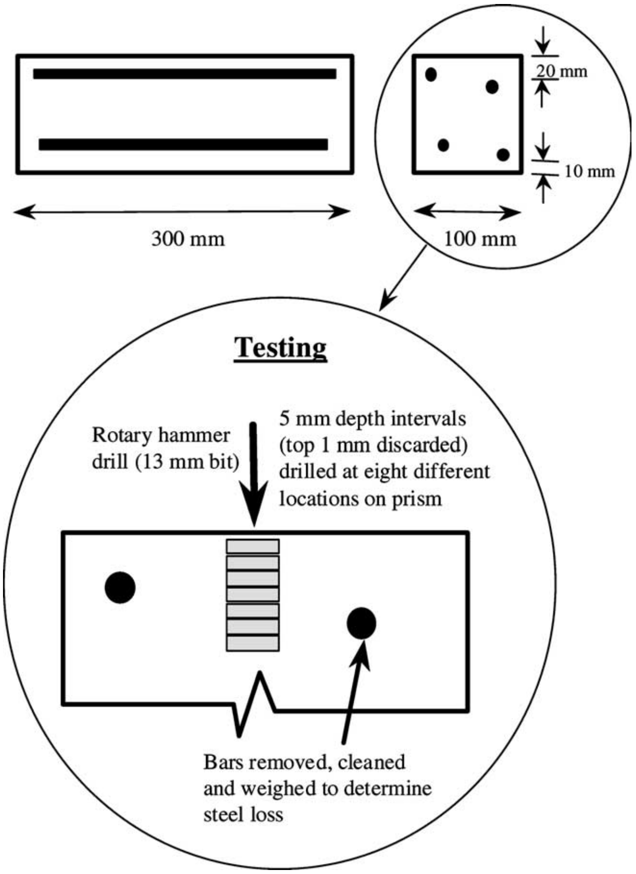


Fig. 1. Details of reinforced concrete specimens (not to scale).

3. Results

3.1. Compressive strength

Table 4 shows the compressive strength results for concrete cubes from the G, A and H series after 2 and 10 years exposure in the marine tidal zone. Also shown is

Table 4
Strength results (MPa) for marine-exposed concretes after 2 and 10 years exposure

Nominal strength grade	Exposure period (years)	Pfa content					
		OPC	15% P1	30% P1	50% P1	30% P2	30% P3
C25	2	31.5	35.7	43.8	41.7	44.2	43.0
	10	22.7	32.1	41.5	54.1	43.6	45.6
	10/2 (%)	72	90	95	130	99	106
C35	2	48.2	53.8	57.2	56.9	58.2	55.8
	10	–	43.4	55.8	62.7	63.0	55.3
	10/2 (%)	–	81	98	110	108	99
C45	2	56.5	57.7	63.5	61.2	64.2	63.2
	10	52.5	59.8	68.2	68.0	69.3	65.9
	10/2 (%)	93	104	107	111	108	104

the strength at 10 years as a proportion of the 2-year strength. Two of the three concretes without pfa lost strength between 2 and 10 years, particularly the lower strength C25 mix (no cubes were available at 10 years for the C35 PC concrete). The lower grade concretes with 15% pfa also exhibited some degree of strength loss between 2 and 10 years, although the extent of the loss was less than that observed for the PC concrete. Concrete with 30% pfa showed mixed behaviour with the strength at 10 years ranging from 95% to 108% of the 2-year strength. Concrete with 50% pfa showed increased strength between 2 and 10 years, with an increase as high as 30% in one case.

Some degree of strength loss may be expected in this environment as none of the concretes were air-entrained. However, any visible evidence of damage was not generally consistent with frost damage, but took the form of softening of the surface layers; this was particularly noticeable for the lower grade PC concrete. Little visible damage was observed for concrete with more than 15% pfa. Microstructural observations revealed that the weakening of the surface layer in the PC concrete was attributable to chemical attack, predominantly by sulfates, as shown by the abundance of sulfate minerals, including thaumasite, in the affected concrete. This has been discussed in detail in an earlier paper [11].

3.2. Chloride penetration

The initial moist-curing period and subsequent early-age storage conditions were found to have a pronounced effect on the permeability and rate of carbonation of companion specimens stored in other environments [12,13]. However, curing history did not have a consistent effect on the chloride penetration data for specimens stored in this marine environment [3] and it is suggested that this is due to continued curing during seawater exposure which masked the differences due to early treatment. Consequently, most of the data presented in this paper refer to specimens that were initially cured for 1 or 3 days.

Chloride concentration profiles for C25 and C45 concretes are shown in Figs. 2 and 3 respectively. It is

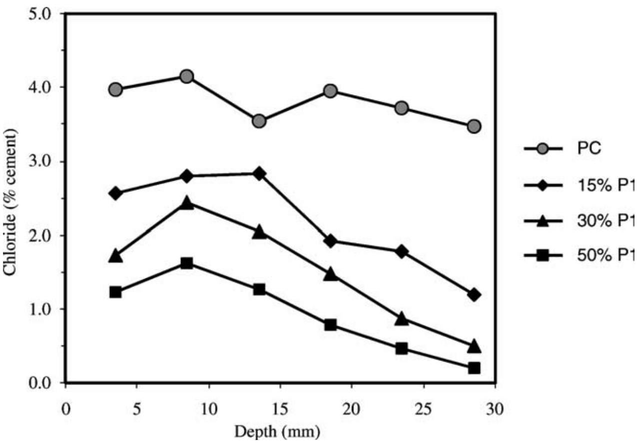


Fig. 2. Effect of pfa on chloride profiles at 10 years—C25 concretes.

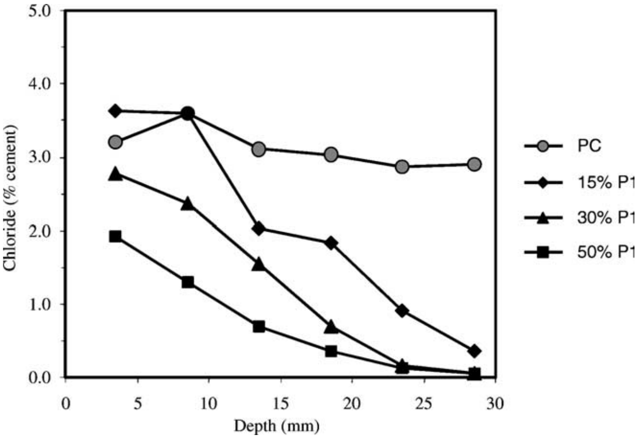


Fig. 3. Effect of pfa on chloride profiles at 10 years—C45 concretes.

clear that pfa has a pronounced effect on the profiles and that its presence significantly increases the resistance of the concrete to chloride ion penetration. Pfa was effective in reducing the chloride concentration at all depths, but the effects become more apparent (and more significant) with increased depth. The PC concretes tested in this study clearly offer very little long-term resistance to chloride penetration and the profiles are relatively flat even in the higher grade concrete (C45) where the free water/cement ratio was approximately 0.49.

The relative influence of strength grade and pfa content on chloride ingress can be seen in Fig. 4. Increasing the strength grade from C25 to C35 has no significant impact on the 10-year chloride profile in PC concrete and a further increase to C45 only has a marginal effect in reducing the amount of chloride ingress. It is apparent that the incorporation of 30% pfa is far more effective than increasing the strength of the PC concrete within the range tested in this programme.

Three pfas were tested in this programme and the chloride profiles for C35 concretes after 10 years exposure are compared in Fig. 5. There appears to be some small effect due to the nature of the pfa with ash P3 providing the greatest resistance to chloride penetration and P1 the lowest. However, these trends were not observed consistently within the other strength grades (for the C45 concretes the ranking order was reversed) and are more likely to be due to experimental variations than any inherent property of the ashes.

Figs. 6 and 7 show the influence of the initial storage conditions on the chloride profiles at 10 years for C35 concretes with 0% and 30% pfa respectively. As noted above, the temperature and humidity of the storage conditions prior to marine exposure did not consistently alter the performance of the concrete with regard to chloride ion penetration. As with the moist-curing period, it is suspected that the effects of continued exposure to moisture during long-term exposure masked the early treatment of the concrete samples. For this reason, the remainder of the discussion will concentrate on the G, A and H series of concretes initially stored at 20 °C and 65%rh, in particular to enable the influence of concrete grade and pfa content to be explored.

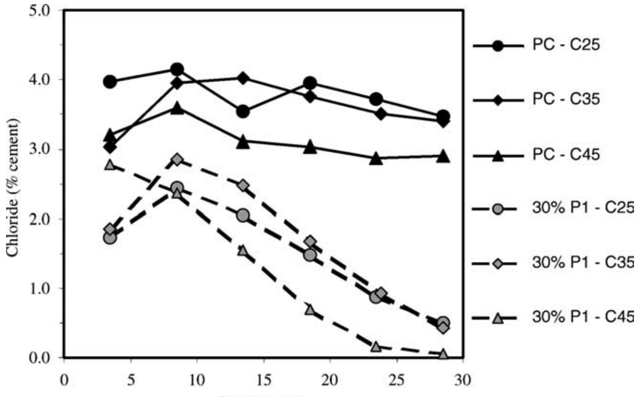


Fig. 4. Effect of strength grade on chloride profiles at 10 years—concretes with 0% and 30% pfa (P1).

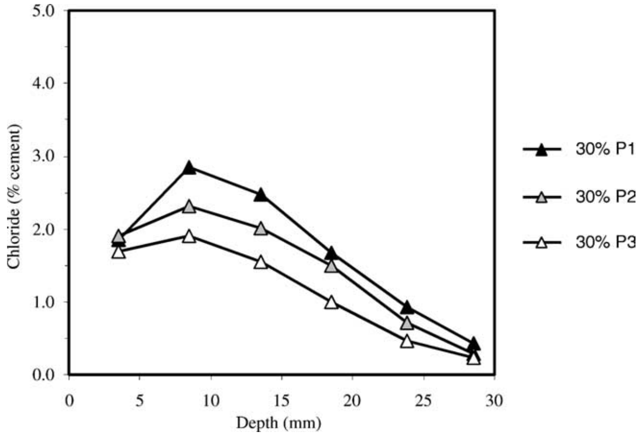


Fig. 5. Effect of pfa source on chloride profiles at 10 years—C35 concretes.

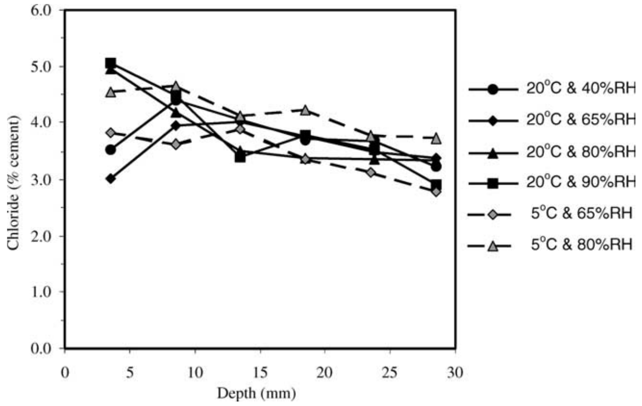


Fig. 6. Effect of initial storage conditions on chloride profiles at 10 years—C35 PC concretes.

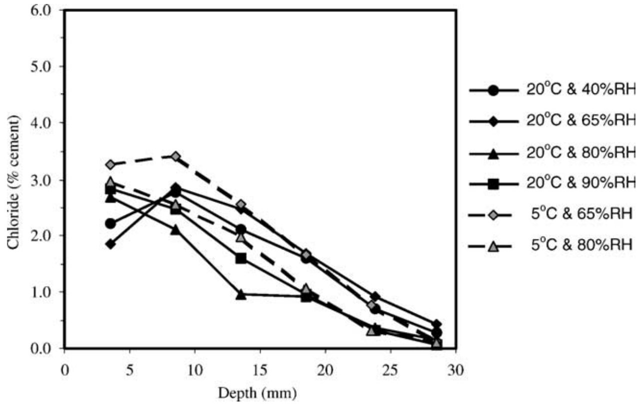


Fig. 7. Effect of initial storage conditions on chloride profiles at 10 years—C35 concretes with 30% pfa (P1).

Chloride profiles established after different periods of exposure are shown in Figs. 8 and 9 for the C35 concretes with 0% and 30% pfa respectively. Differences between the concretes with and without pfa are generally less noticeable at early ages (e.g. 1 and 28 days). During this period much of the chloride ingress is probably due to capillary suction as the concrete samples were unsaturated when they were placed in the tidal zone, so that the seawater would have been rapidly absorbed into the concrete specimens. After the initial saturation by seawater the bulk of the concrete would be expected to remain in a saturated condition during the remainder of the exposure period. Evaporation of moisture from the specimens during low tide would be minimal as the specimens were protected from both direct sunlight and wind. Thus, beyond the very early period, ionic diffusion is expected to be the predominant transport mechanism in the saturated concrete. The incorporation of pfa clearly decreases the diffusivity of the concrete and this effect appears to become more pronounced with age.

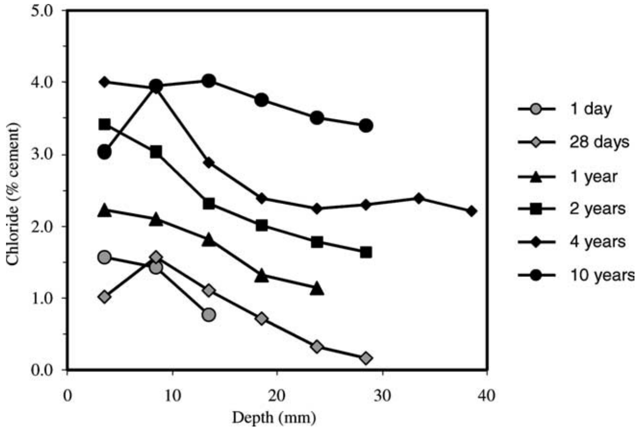


Fig. 8. Effect of exposure period on chloride profiles—C35 PC concretes.

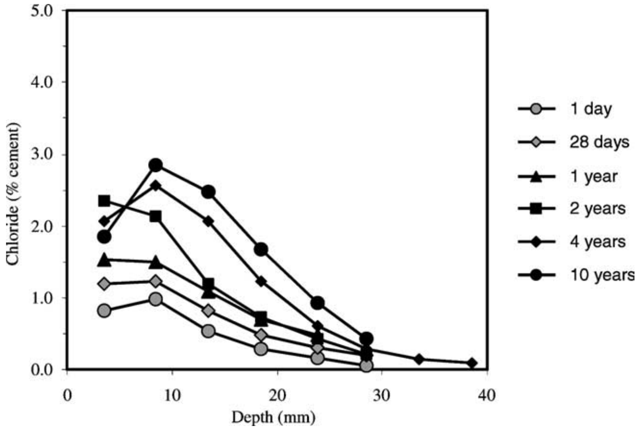


Fig. 9. Effect of exposure period on chloride profiles—C35 concretes with 30% pfa (P1).

It is interesting to note from Figs. 8 and 9 that the chloride concentration at the surface (a parameter used in service life modelling to characterize the severity of the exposure environment) changes significantly over the 10-year period in the tidal zone, for concretes both with and without pfa.

Perhaps the most significant factor in these tests is how quickly the chlorides accumulate at depth in the concrete, i.e. at locations where reinforcing steel may be encountered, rather than how the surface concentration changes. Fig. 10 shows the rate of chloride build up with time at the depth interval 21–26 mm for C35 concrete. This depth interval was selected as it is the deepest interval for which complete data were collected at all ages. The concentration is shown plotted against the square root of time. Beyond the first 28 days, differences between the concretes are quite remarkable. After 10 years exposure, the chloride content in this interval is 3.50% (by mass of cement) in the control PC concrete and only 0.42% in the concrete with 50% pfa.

Fig. 11 shows the chloride content in the 21–26 mm depth interval after 10 years exposure as a function of strength grade and pfa content. The increase in strength grade from C25 to C35 had surprisingly little impact on this value in the concretes with or without pfa. Further increase to C45 results in significant reduction, but it is evident that the effect of strength grade (in the range studied) is secondary to that of pfa content.

Fig. 12 shows the chloride content in the 21–26 mm depth interval after 10 years exposure plotted against the water to cementitious material ratio, $W/(C+P)$. At a given $W/(C+P)$ the extent of chloride penetration decreases as the proportion of pfa (P) increases in the cementitious blend. This means that pfa and cement do not have equivalent performance with respect to chloride resistance. In other words, although an efficiency factor for pfa of $k = 0.3$ was sufficient for achieving similar

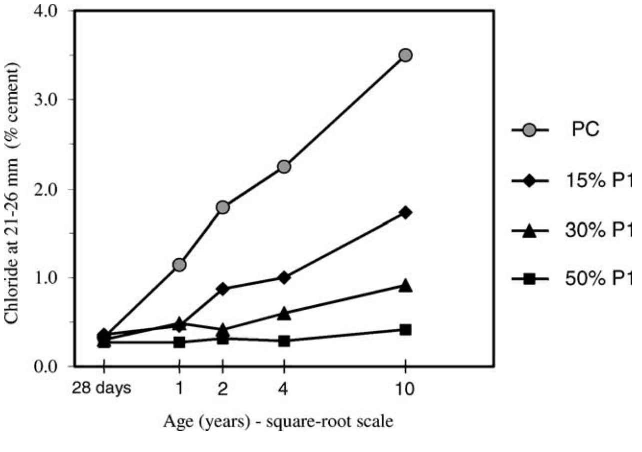


Fig. 10. Effect of pfa on rate of chloride build up in the 21–26 mm depth interval—C35 PC concretes.

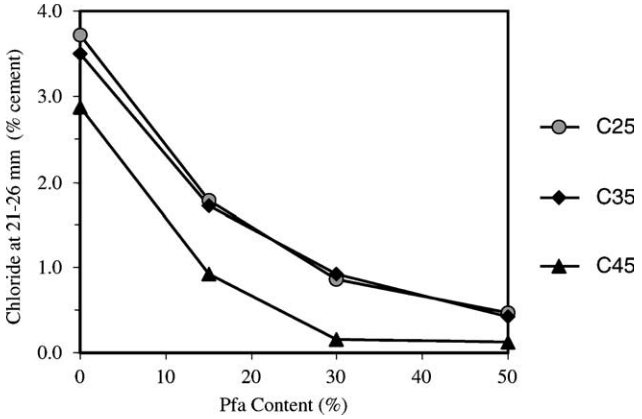


Fig. 11. Effect of strength grade on chloride in the 21–26 mm depth interval—10 years exposure.

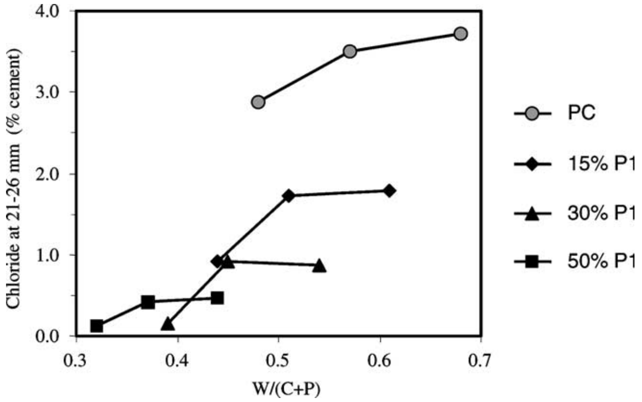


Fig. 12. Effect of water–cement ratio on chloride in the 21–26 mm depth interval—10 years exposure.

strength at 28 days, the value of *k* is clearly greater than unity when the performance of the pfa is measured in terms of chloride resistance.

Another approach to analyzing these data is to determine the rate of penetration of some critical chloride concentration. For instance, if it is assumed that some level of chloride, C_{thresh}, represents the amount of chloride required to initiate corrosion of the embedded steel, then plotting C_{thresh} against depth will indicate how the time to corrosion initiation varies with cover depth for a particular concrete. Analysis of the 4-year data from the current programme [4,6] indicated that chloride threshold values may decrease with increasing pfa content. The values determined are given in Table 5. Threshold concentrations could not be calculated from the 10-year data in the same manner as they were from the 4-year data because *all* rebars were showing signs of corrosion at 10 years, and thus a distinction between corroding and non-corroding rebars could not be made.

Table 5
Chloride threshold values calculated from 4-year marine exposure data

Pfa content (%)	Threshold total chloride level (% by mass of cement plus pfa)
0	0.70
15	0.65
30	0.50
50	0.20

In most cases, the depth of penetration of C_{thresh} could be interpolated from the concentration profiles. The exception to this was for the values for the PC concretes beyond 28 days. In these cases, the depth of the threshold value had to be extrapolated from the profiles by fitting Eq. 1 (see below) to the experimental data. Fig. 13 shows the rate of penetration of the chloride level C_{thresh} for the C35 concretes. The C_{thresh} values used were those presented in Table 5, i.e. C_{thresh} decreases with increasing pfa content. No values are given for the PC concrete for ages beyond 2 years because the chloride profiles were increasingly affected by penetration from adjacent faces of the specimens.

Although the individual values of C_{thresh} for the different pfa levels were used to produce Fig. 13, a chloride threshold level of 0.40% is frequently quoted as a 'universal' value. It is clear, however, that true threshold values will be dependent on a number of parameters. For example, according to Hobbs and Matthews [14], the total critical chloride ion concentration increases as the binding of chlorides increases, as the hydroxyl ion concentration increases, as the degree of water saturation increases and as the water/cement ratio decreases. The cement type will clearly have an influence on some of these parameters and different values for C_{thresh} could be expected for different cement types, as shown by the values given in Table 5. Corresponding to Fig. 13, the rate of penetration of the chloride level $C_{\text{thresh}} = 0.40\%$ (by mass of cement) for the C35 concretes is shown in Fig. 14.

The similarity between Figs. 13 and 14 can immediately be seen and, whether taking the determined value of C_{thresh} of 0.70% or the 'universal' value of 0.40%, the data indicate that the threshold value advances rapidly through the C35 PC concrete. Corrosion initiation

Fig. 13. Effect of pfa on the depth of penetration of the threshold concentration C_{thresh}.

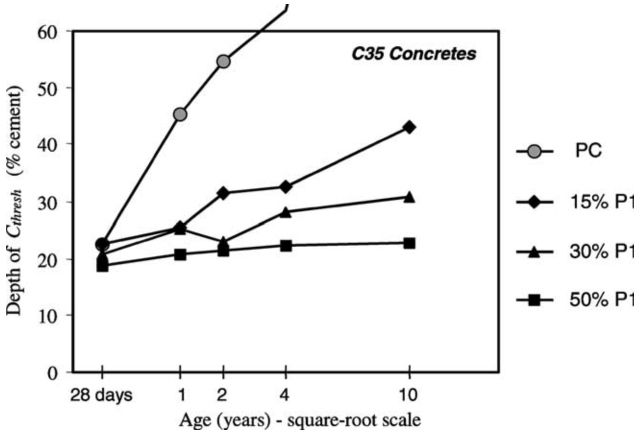


Fig. 14. Effect of pfa on the depth of penetration of the threshold concentration $C_{\text{thresh}} = 0.4\%$ (by mass of cement).

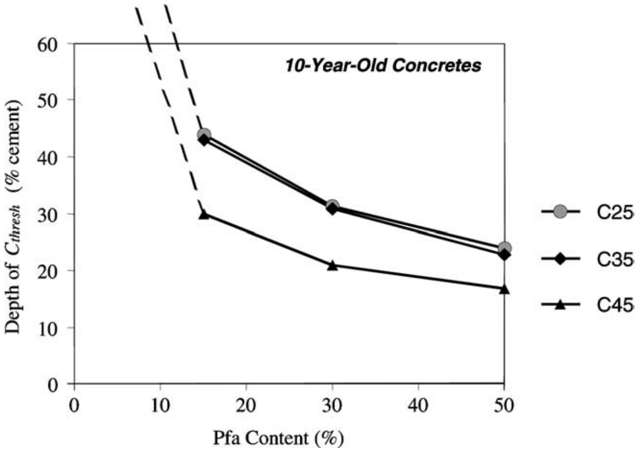


Fig. 15. Effect of strength grade on the depth of penetration of the threshold concentration $C_{\text{thresh}} = 0.4\%$ (by mass of cement).

would occur after just a few years even if the steel was provided with concrete cover in the range of 40–60 mm. In the pfa concrete, after the initial rapid penetration of chlorides during resaturation by sea water, the rate of penetration is comparatively slow and decreases with increasing pfa content. The main difference between Figs. 13 and 14 is that for 50% pfa the depth of penetration of C_{thresh} at 28 days is about 25 mm when the determined value of C_{thresh} of 0.20% is used, compared with about 19 mm when the 'universal' value of 0.40% is used. Thereafter, however, the rate of increase is equally low and the threshold only progresses a further 4 mm into the concrete during the next 10 years in the tidal zone. For concrete with 30% pfa the initial (28 days) penetration is 18–21 mm with a total penetration of just 28–31 mm after 10 years, the depths again depending upon the value of C_{thresh} that is used. It is apparent that these pfa concretes could confer long-term protection to the steel provided adequate cover was afforded.

Fig. 15 shows the depth of penetration of the threshold chloride level, $C_{\text{thresh}} = 0.40\%$, as a function of pfa content and strength grade. As with previous observations, the increase in grade from C35 to C45 provides some level of increased resistance to chloride penetration, but the effect of adding pfa is much more marked.

3.3. Determination of chloride diffusion coefficients

A now commonly used approach for determining diffusion coefficients from concentration profiles is to fit Crank's solution [15] to Fick's second law of diffusion; the solution being:

$$\frac{C_{x,t}}{C_s} = 1 - erf\left(\frac{x}{2\sqrt{D_a t}}\right) \quad (1)$$

where: $C_{x,t}$ = chloride concentration at depth x after time t; C_s = chloride content at the surface; D_a = apparent diffusion coefficient.

Generally, "best-fit" values of C_s and D_a are found by iteration using least squares. Typical values obtained for the profiles measured in this study are given in Table 6. As would be expected the coefficient decreases with increasing strength grade, pfa content and, to a lesser extent, exposure period. Using this approach for the current study has the following limitations:

- Specimens were unsaturated at the time of exposure and significant chloride ingress occurs due to capillary suction
- The surface concentration changes with time (i.e. $C_s = f_1(t)$), probably as a result of wetting and drying cycles in the surface zone
- The apparent diffusion coefficient tends to decrease with time (i.e. $D_a = f_2(t)$)
- Some of the profiles are affected by chloride penetration from the orthogonal face (particularly those for PC concrete) and a two-dimensional analysis should be used.

In most situations in practice, one or more of the above limitations might be expected to apply, especially in highway structures periodically exposed to de-icing salts. However, it has become commonplace to use this approach to determine diffusion coefficients in existing structures and extrapolate the data to predict the time to the onset of corrosion [16,17].

Previous papers [4,5] have reported the development and use of a numerical model, using a direct finite difference implementation of Fick's second law, to allow for the initial sorption effects, changing surface concentration and two-dimensional ingress. It has not yet been possible to apply such a detailed analysis to the 10-year data, and the diffusion coefficients quoted in Table 6 were determined by fitting Crank's solution to Fick's second law. Each value, therefore, as a 'best fit' to

Table 6
Diffusion coefficients calculated from concentration profiles using Crank's solution (Eq. 1)

Strength grade	Pfa (% P1)	Diffusion coefficient (10^{-13} m^2/s)			
		1 year	2 years	4 years	10 years
C25	0	–	153	162	*
	15	–	33.6	23.9	9.94
	30	–	33.4	16.7	5.52
	50	–	24.6	24.8	4.22
C35	0	156	92.9	56.6	*
	15	51.0	29.2	14.8	9.05
	30	53.5	16.0	10.9	4.49
	50	38.7	19.8	9.41	3.45
C45	0	–	44.7	63.9	*
	15	–	18.3	13.0	5.42
	30	–	14.4	5.84	2.01
	50	–	14.5	8.47	2.00

* Diffusion coefficients were not calculated (profiles dominated by 2-D ingress).

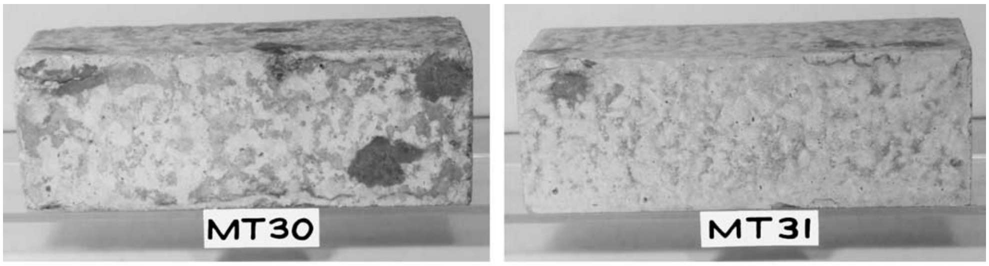
the experimental data, can be considered as an average value over the whole of the corresponding time period with no account taken of initial sorption and no attempt to quantify diffusion coefficients over intermediate periods, e.g. between 2 and 4 years.

The more detailed analysis of the earlier results, reported for PC concrete and concrete with 50% pfa [4], showed that correcting for initial sorption effects produced little change in the calculated diffusion coefficient for PC concrete but a considerable reduction in the calculated coefficients for concrete with 50% pfa. The results indicated that the 28-days profile accounted for a significant proportion of the chloride present after 4 years exposure for the concrete with 50% pfa. Consequently, the assumption that these chlorides penetrated by diffusion rather than sorption introduced considerable error in the diffusion coefficient calculated from concentration profiles. The initial sorption profile became less significant for long-term profiles in concrete with higher diffusivity (i.e. PC concrete). Similar conclusions can be reached from the 10-year data from studying Fig. 10. This shows the very small increase in chloride concentration in the 21–26 mm depth interval beyond 28 days for the concrete with 50% pfa and also illustrates that the chloride present at 28 days in the PC concrete is a small proportion of that present at later ages.

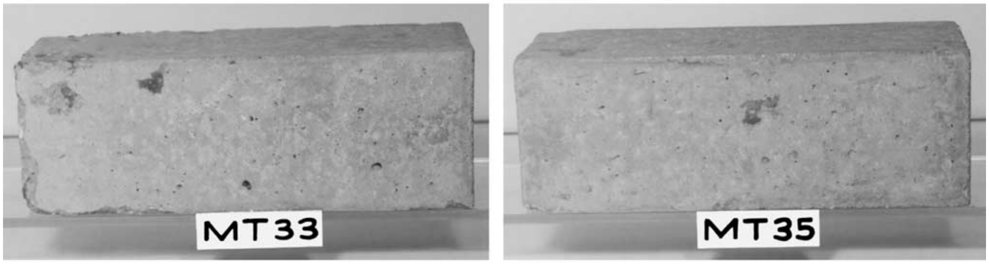
3.4. Reinforcement corrosion

Fig. 16 shows photographs of the C35 concrete prisms recovered after 10 years exposure. The degree of rust staining can be seen to reduce as the pfa content increases. Fig. 17 shows the steel reinforcing bars recovered from these concretes at 10 years prior to their being cleaned for weight loss determination. Although the bars with 10 mm cover from all of the concretes are showing significant corrosion, it can be seen that the amount of corrosion on the bars with 20 mm cover decreases as the pfa content increases. These observations are entirely consistent with expectations based on the discussion of the chloride penetration data.

For the C35 concretes, the percentage loss of rebar mass with time is shown for the 10 mm cover bars in Fig. 18 and for the 20 mm cover bars in Fig. 19. In each case, the mass loss is greatest for the PC concrete, whilst the 10 mm cover bars from the concrete with 15% pfa also showed significant mass loss. For the concretes with



(a) PC – no pfa (b) 15% pfa (P1)



(c) 30% pfa (P1) (d) 50% pfa (P1)

Fig. 16. Photographs of concrete specimens after 10 years exposure—C35 concretes.

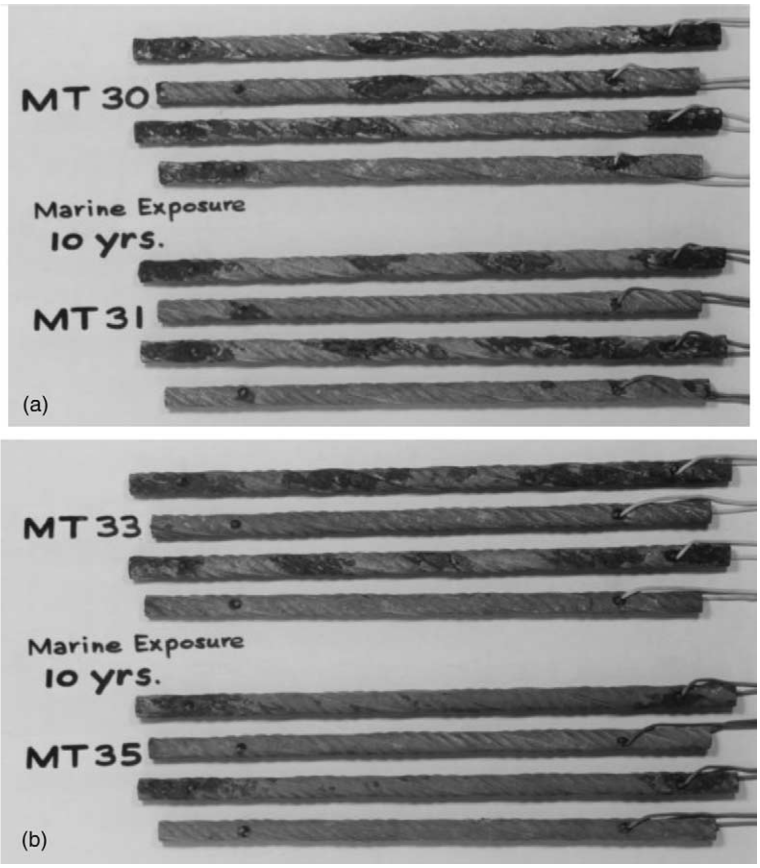


Fig. 17. Reinforcing bars (recovered from concrete) after 10 years exposure—C35 concretes. (a) Rebars extracted from concrete with 0% pfa (top) and 15% pfa (bottom). (b) Rebars extracted from concrete with 30% pfa (top) and 50% pfa (bottom). Long bars had 10 mm cover and short bars had 20 mm cover. Note the absence of corrosion on the 20 mm cover bars from the concretes with 30% and 50% pfa.

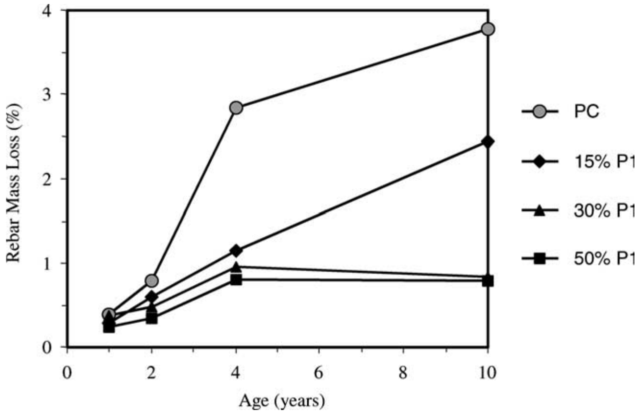


Fig. 18. Effect of pfa on the rate of corrosion—C35 concrete with 10-mm cover.

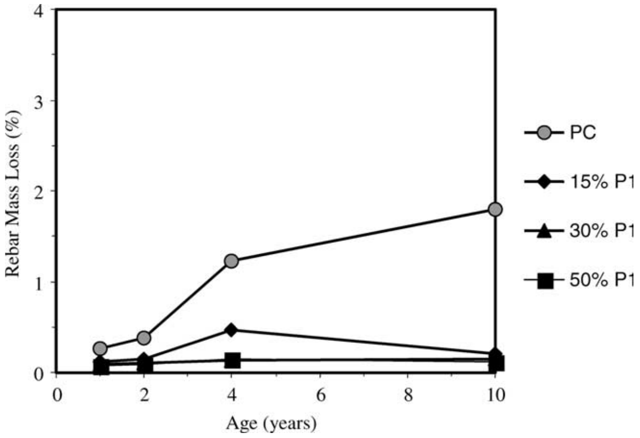


Fig. 19. Effect of pfa on the rate of corrosion—C35 concrete with 20-mm cover.

30% and 50% pfa, however, mass losses were small from the 10 mm bars and almost negligible from the 20 mm cover bars, especially when the average processing mass loss of 0.09% [4] is subtracted from the values plotted in Fig. 19. It is also noteworthy that the mass losses of rebars from the concretes with 30% and 50% pfa showed no increase between 4 and 10 years, consistent with the small increases in chloride levels between 4 and 10 years for these concretes (see Figs. 9, 10, 13 and 14).

The effects of pfa content and concrete strength grade on rebar mass loss at 10 years are shown for the 10 and

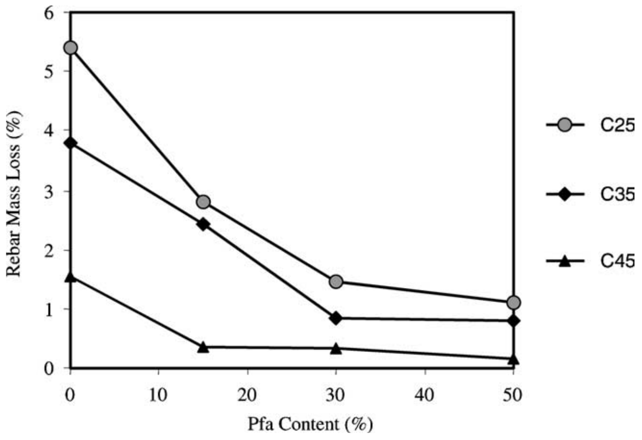


Fig. 20. Effect of pfa content and strength grade on the amount of corrosion at 10 years—10 mm cover.

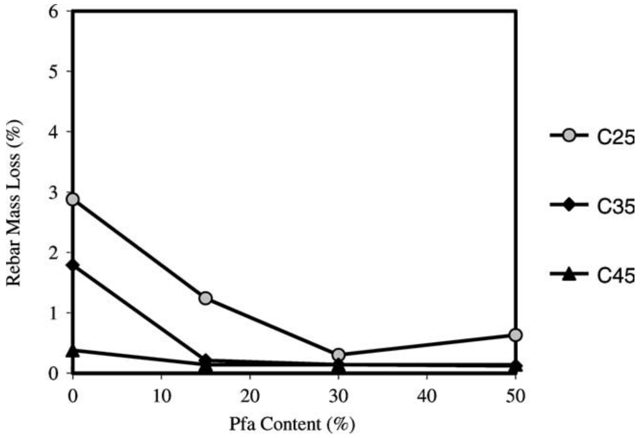


Fig. 21. Effect of pfa content and strength grade on the amount of corrosion at 10 years—20 mm cover.

20 mm cover bars in Figs. 20 and 21 respectively. Both the rapid decline in mass loss with increasing pfa content and the relatively smaller decreases with increasing concrete grade can be observed in these figures. These trends are consistent with the relative influences of pfa content and concrete grade on chloride levels (see Figs. 4 and 11), with pfa content having the greater effect.

4. Discussion

The beneficial effect of pfa on both chloride penetration and reinforcement corrosion has again been demonstrated by these long-term data. Even though the data obtained after 4 years exposure to marine conditions indicated decreasing chloride threshold concentrations with increasing pfa content [4,5], this trend is clearly more than offset by the greatly improved resistance to chloride penetration, as evidenced by the decreasing rates of corrosion with increasing pfa content.

Although all of the concretes, with or without pfa, experienced an initial penetration of chlorides due to absorption by the unsaturated specimens, subsequent chloride penetration appears to be diffusion controlled. Whereas chloride levels were found to rise significantly in the PC concrete at each test age, increases of chloride levels in the pfa concretes were small in comparison and became progressively smaller with increasing pfa content. Chloride diffusion coefficients for both PC and pfa concretes decrease with time and with increasing pfa content (see Table 6). The values for the PC concrete are, however, considerably higher than those for the pfa concretes. This is illustrated in Fig. 22 in which the variation of diffusion coefficients with time is plotted.

The superiority of pfa concretes over PC concretes in terms of resistance to chloride-induced corrosion of reinforcement has not been recognised in British Standards which, until now, have recommended similar concrete parameters, including minimum strength grade, for a given exposure condition irrespective of cement type. However, the advent of the European Standard for concrete, the English language version of which is now published as BS EN 206-1 [18], has led to a re-examination of UK recommendations which will go some way towards correcting this situation.

The current British Standard for concrete, BS 5328 [19], defines exposure conditions in terms of five classes ranging in severity from mild to most severe, together with a further class for abrasion. Seawater tidal zone conditions are classed as 'most severe' exposure and the recommended concrete parameters are: maximum free W/C 0.45, minimum cement content 400 kg/m^3, minimum grade C50. If the concrete is subject to freezing whilst wet, air entrainment should be used and a reduction of one grade is permitted. In addition, BS 8110 [20] gives the nominal cover to reinforcement for these exposure conditions as 50 mm.

Exposure conditions are defined in BS EN 206-1 in terms of the potential mode of deterioration of

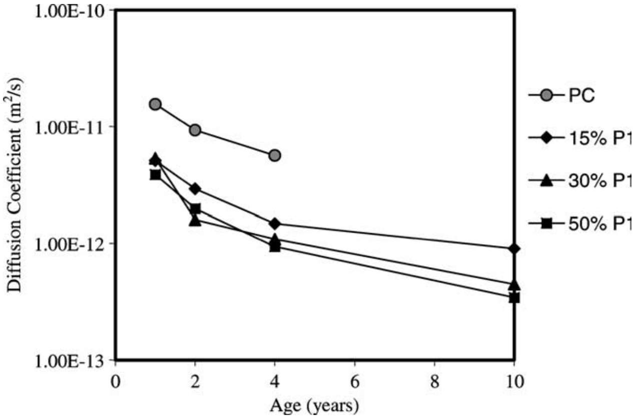


Fig. 22. Variation of diffusion coefficients with time.

concrete—thus, there are exposure classes for carbonation-induced corrosion, corrosion induced by chlorides from seawater, corrosion induced by chlorides from other sources, freeze–thaw attack and chemical attack, giving a total of 18 exposure classes. The concrete parameters given for each of these exposure classes are, however, only recommended values and national values are permitted to be used.

Since the current British Standard for concrete, BS 5328, only defines exposure conditions in terms of six classes, it has become necessary for the recommended concrete parameters to be re-examined in the light of the European exposure classes. This has been carried out in order to provide recommendations for inclusion in a new British Standard, BS 8500 [21], which is complementary to BS EN 206-1 and, together with BS EN 206-1, will co-exist with BS 5328 until 1 December 2003 when the latter standard will be withdrawn. In drafting BS 8500, differences in performance of different cement types have been taken into account where applicable. The recommendations in BS 8500 for exposure classes concerned with corrosion of reinforcement induced by chlorides from sea water recognise that concretes containing pfa or ground granulated blastfurnace slag (GGBS) perform better than PC concretes in such conditions by allowing less onerous concrete parameters.

The exposure classes in BS 8500 are, with one or two exceptions, as defined in BS EN 206-1 but the informative examples of each exposure class have been tailored more to UK conditions. BS 8500 defines the classes relevant to corrosion induced by chlorides from seawater (XS classes) as follows:-

Class designation	Class description	Informative examples applicable in the UK
XS1	Exposed to airborne salt but not in direct contact with sea water	External reinforced and prestressed concrete surfaces in coastal areas
XS2	Permanently submerged	Reinforced and prestressed concrete completely submerged and remaining saturated, e.g. concrete below mid-tide level
XS3	Tidal, splash and spray zones	Reinforced and prestressed concrete surfaces in the upper tidal zones and the splash and spray zones

It is recognised that XS3 exposure can cover a range of conditions, the most extreme being in the spray zone and the least extreme in the tidal zone where conditions can be similar to XS2 i.e. saturated. BS 8500 makes the following recommendations for reinforced concrete to be exposed in exposure classes XS2 and XS3 for an intended working life of at least 50 years. These recommendations are intended to take into account the most extreme conditions within the XS3 class:-

Exposure class	Nominal cover[a] (mm)	Minimum strength class[b]	Maximum W/C ratio	Minimum cement content (kg/m^3)	Cement/combination types[c]
XS2	$40 + \Delta c$	C28/35	0.55	320	PC, SRPC, pfa (6–20%), ggbs (6–35%)
		C25/30	0.55	320	pfa (21–35%), ggbs (36–65%)
		C20/25	0.55	320	pfa (36–55%), ggbs (66–80%)
XS3	$50 + \Delta c$	C40/50	0.40	380	PC, SRPC, pfa (6–20%), ggbs (6–35%)
		C28/35	0.50	340	pfa (21–35%), ggbs (36–65%)
		C25/30	0.50	340	pfa (36–55%), ggbs (66–80%)
	$45 + \Delta c$	C45/55	0.35	380	PC, SRPC, pfa (6–20%), ggbs (6–35%)
		C32/40	0.45	360	pfa (21–35%), ggbs (36–65%)
		C28/35	0.45	360	pfa (36–55%), ggbs (66–80%)
	$40 + \Delta c$	C35/45	0.40	380	pfa (21–35%), ggbs (36–65%)
		C32/40	0.40	380	pfa (36–55%), ggbs (66–80%)

[a] Expressed as the minimum cover to reinforcement plus a tolerance, Δc, to accommodate fixing precision.

[b] BS EN 206-1 nomenclature: characteristic compressive strength at 28 days of cylinders (150 × 300 mm)/cubes (150 mm).

[c] Other cement types are included in the PC grouping (e.g. silica fume, metakaolin and Portland limestone) but are not considered further in this paper.

Where other mechanisms of potential concrete deterioration are identified, e.g. carbonation-induced corrosion or freezing and thawing, the concrete parameters relevant to each exposure class must be compared and the most onerous values selected. No recommendations are given for an intended working life of at least 100 years in chloride environments because BS 8500 states that the spread of data from research and surveys of actual structures does not permit precise recommendations for concrete cover to be given. As a first estimate, however, an increase in cover by 15 mm from values given in the above table is suggested.

The following table compares the BS 8500 recommendations for XS3 exposure, for 45 mm minimum cover (plus tolerance), with the corresponding values in the current BS 5328 and BS 8110 (i.e. for 50 mm nominal cover) where no distinction is made between cement types. It can be seen that, in general, the parameters for PC have become more onerous in BS 8500 whilst those for pfa and ggbs concretes have become less onerous:-

Standard	Nominal cover (mm)	Minimum strength class	Maximum W/C ratio	Minimum cement content (kg/m^3)	Cement or combination types
BS5328/ BS8110	50	C50	0.45	400	All
BS 8500	$45 + \Delta c$	C45/55	0.35	380	PC, SRPC, pfa (6–20%), ggbs (6–35%)
		C32/40	0.45	360	pfa (21–35%), ggbs (36–65%)
		C28/35	0.45	360	pfa (36–55%), ggbs (66–80%)

The British Standard for maritime structures [22], BS 6349, has also been recently revised and, although the exposure classes are also based on those given in BS EN 206-1, there are differences from BS 8500. Exposure classes and exposure conditions in the UK are given as follows:-

Exposure conditions in the UK	Exposure class	
Airborne salt		XS1
Frequently wetted	Submerged	XS2
	Lower tidal, back-filled	XS2/XS3
Infrequently wetted.	Upper tidal, splash/spray, “dry” internal faces of submerged structures	XS3

The corresponding recommendations for concrete qualities and cover for a required design working life of 50 years are as follows:-

Exposure class	Minimim cover[a] (mm)	Minimum strength class	Maximum W/C ratio	Minimum cement content (kg/m^3)	Cement/combination types
XS2	40	–	–	–	PC, SRPC, pfa (<55%), ggbs (<80%)
XS2/XS3	50	–	0.50	360	PC, SRPC, pfa (<55%), ggbs (<80%)
XS3	60	C40/50	0.40	400	PC, SRPC, pfa (<20%), ggbs (<35%)
	50	C30/37	0.50	360	20 < pfa < 55%, 35 < ggbs < 80%
	40	C25/30	0.50	360	35 < pfa < 55%, 50 < ggbs < 80%

[a] Excludes tolerance to be added to minimum cover to derive the nominal cover.

BS 6349 also gives recommended limiting values for concrete parameters for a required design working life of 100 years but these will not be considered in the present discussion. It can be seen that, for XS3 exposure, PC would not be permitted for minimum covers less than 60 mm and even in the less onerous XS2/XS3 class a minimum cover of 50 mm would be required. As with BS 8500, the requirements for pfa and ggbs concretes become less onerous with increasing pfa or ggbs contents.

It can be seen from the above Tables that, in both BS 8500 and BS 6349, higher maximum W/C ratios and lower minimum cement contents are permitted for cement types containing sufficient quantities of pfa or ggbs compared with PC. In addition, lower minimum strength grades are permitted, thus recognising that concretes made with such cements will have lower strengths compared with PC concrete of equal W/C ratio and obviating the previously implied need to use *lower* W/C ratios or *higher* cement contents than corresponding PC concretes in order to achieve a given strength.

In assessing the results from the current programme, it is recognised that the cover depths employed were only 10 and 20 mm (in order to induce some corrosion within a reasonable time span) and the qualities of some of the concretes tested were below those given in BS 8500. For example, the highest grade PC concrete tested was C45 and this had an approximate free W/C ratio of 0.49 and a cement content of 350 kg/m^3 and would therefore have failed to meet the BS 8500 requirements in all respects. Of the pfa concretes tested, those with 15% pfa also failed to meet the BS 8500 requirements at all strength grades; for 30% pfa, the C35 concretes met the relevant requirements for 50 mm cover and the C45 concretes met the requirements for 40 mm cover and above; for 50% pfa, the C35 and the C45 concretes all met the requirements for 40 mm cover and above. Nevertheless it is clear from examination of Fig. 12, which shows the concentration of chloride in the 21–26 mm depth interval after 10 years exposure plotted against W/C ratio, that a higher chloride level would be expected at this depth in a PC concrete of W/C ratio 0.40 than in a concrete containing 30% pfa and with W/C ratio 0.50.

A further significant comparison can be made from Figs. 2 and 3 where it can be seen that chloride levels at all depths, and especially at depths >20 mm, are much lower in the C25 concretes with 30% and 50% pfa than in the C45 PC concrete. This is not entirely reflected in the corresponding degrees of corrosion, however, since the rebars at 10 and 20 mm cover depths from the C25 pfa concretes with 30% and 50% pfa have suffered similar weight losses to those from the C45 PC concrete (see Figs. 20 and 21). This will be partly due to the fact that there are smaller differences in the chloride profiles at these low depths (i.e. 10 and 20 mm) and also reflects the lower chloride threshold values for these pfa concretes. It is also clear that the 10-year PC concrete chloride profiles are affected by chloride penetration from adjacent specimen faces.

Perhaps the most encouraging result from the point of view of the PC concrete is that, for the C45 grade (less than the minimum grade of C40/50 permitted by BS 8500 for PC concrete in XS3 conditions) very little corrosion was observed on the bars with 20 mm cover after 10 years exposure (see Fig. 21) whereas the minimum cover corresponding to grade C40/50 in the BS requirements would be 50 mm. Examination of Fig. 3, however, indicates that there is a high chloride concentration in the depth intervals adjacent to the 20 mm cover rebar so that the lack of corrosion is surprising. In Fig. 23, rebar weight loss is plotted against chloride content at the location of the bar for all concretes, taking the chloride content in the 11–16 mm depth interval as appropriate for the 10 mm cover bars and the chloride content in the 21–26 mm depth interval as appropriate for the 20 mm cover bars. The point on Fig. 23 which relates to the 20 mm cover bar from the C45 PC concrete is seen at 2.87% chloride and 0.38% weight loss. Examination of this figure suggests that, with a further small increment in chloride content to perhaps 3.5%, a substantial rise in rebar weight loss might be expected. Judging by the rate of increase of the chloride content of the 21–26 mm depth interval for the C45 PC concrete (see Fig. 24), a level of 3.5% chloride in the 21–26 mm depth interval could be expected at about 15 years. The lack of corrosion on the 20 mm cover bars cannot, therefore, be taken as evidence of continuing satisfactory performance of this concrete.

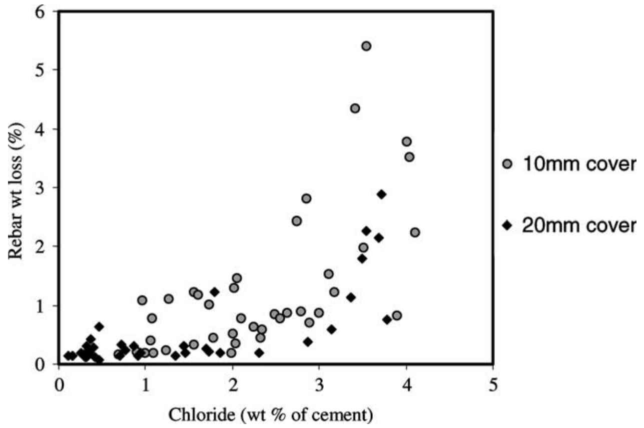


Fig. 23. Rebar weight loss vs. chloride content at the of the bar—10 and 20 mm cover.

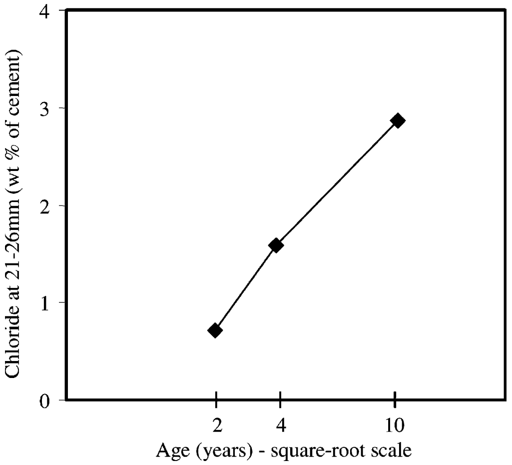


Fig. 24. Rate of increase of chloride in the 21–26 mm depth interval for C45 PC concrete.

Ultimately, because the highest quality PC concrete tested in this programme fell short of that recommended in both the current and new specifications, and because the cover depths chosen were below the recommended minima, it is difficult to predict whether the BS recommendations are sufficiently robust with respect to PC concrete. What is clear, however, is the superior performance in marine tidal conditions of concrete containing 30% or more of pfa and it is encouraging that this superiority has been recognised in the new standards.

5. Conclusions

For concrete specimens of grades C25, C35 and C45 with pfa contents of 0%, 15%, 30% and 50% and exposed for 10 years in marine tidal conditions, the following conclusions can be drawn:

1. Compared with values after 2 years' exposure, compressive strength reductions were observed in the

PC (0% pfa) concretes and, to a lesser extent, in the concretes with 15% pfa. No significant strength losses were experienced by concretes containing 30% or 50% pfa.

2. Chloride levels were reduced significantly in the pfa concretes compared with the PC (0% pfa) concrete, the reductions becoming greater with increasing pfa content.
3. The effect of concrete grade on chloride levels is less marked than the effect of pfa content. An increase in grade from C25 to C35 had only a marginal influence whilst a further increase to C45 produced only a relatively small benefit.
4. The use of three different sources of pfa had only a minor effect on chloride profiles and the differences observed are not thought to be significant.
5. A wide range of early curing and storage regimes was employed but these had little effect on the long-term chloride profiles due to the overwhelming influence of the prolonged exposure to seawater.
6. Because the concretes were not saturated when first exposed to seawater, a considerable degree of absorption of chlorides occurred for all concretes during the first few weeks of exposure. These absorbed chlorides constitute a significant proportion of the total chloride levels observed in the pfa concretes after 10 years exposure, indicating that the quantities of chlorides entering by diffusion are small relative to those entering the PC concrete. This is reflected in the calculated diffusion coefficients which decrease with time, with increasing concrete grade and, especially, with increasing pfa content.
7. The depth of penetration of the threshold chloride concentration for initiating corrosion, C_{thresh}, was plotted against time of exposure for the C35 concretes. Whether using values of C_{thresh} obtained from 4-year data or a ‘universal’ value of 0.40% the data showed that, for concrete with 50% pfa, C_{thresh} only advanced by about 4 mm between 28 days and 10 years, following penetration to a depth of between 19 and 25 mm (depending on the chosen value of C_{thresh}) during the first 28 days exposure due to absorption. In contrast, for the C35 PC concrete, the concentration level C_{thresh} had advanced to an estimated depth of around 50 mm after 2 years exposure.
8. Values of C_{thresh} determined from 4-year data decreased with increasing pfa content, suggesting that greater degrees of corrosion may be observed as the pfa content increases. In fact the reverse is true with rebar weight losses decreasing as the pfa content increases. This indicates that the greatly decreasing chloride diffusion rates more than outweigh the lower chloride threshold values as the pfa content increases.
9. When the performance of the PC concretes is judged in the light of current and new British Standard recommendations for durable concrete it is noteworthy that, for the PC concrete of grade C45 (less than the lowest grade of C40/50 permitted in the new BS for PC concrete in tidal conditions), the rebars with 20 mm cover had suffered only minor weight losses after 10 years exposure. This lack of corrosion, however, cannot be used as evidence to suggest that a C45 PC concrete will have continuing satisfactory performance. This is because the relationship between rebar weight loss and chloride content at the location of the bar, together with the rate of increase in chloride content at this location, suggests that within a further 5 years the degree of corrosion on these bars would have increased significantly.
10. Ultimately, because the highest quality PC concrete tested in this programme fell short of that recommended in both current and potential future specifications, and because the cover depths chosen were below the recommended minima, it is difficult to predict whether the BS recommendations are sufficiently robust with respect to PC concrete. What is clear, however, is the superior performance in marine tidal conditions of concrete containing 30% or more of pfa and it is encouraging that this superiority has been recognised in the new standards.

Acknowledgements

The work described in this paper was supported in the initial stages under a Research Fellowship established at the Building Research Establishment by the former Central Electricity Generating Board in collaboration with Imperial College, London. The later stages of the work were carried out under BRE’s general Government funded programme.

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