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Chloride ingress and strength loss in concrete with different PC–PFA–MK binder compositions exposed to synthetic seawater

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Abstract

The paper reports the influence of the composition of Portland cement (PC)–pulverised fuel ash (PFA)–metakaolin (MK) binders on chloride ingress and strength retardation of PC–PFA–MK concrete exposed to synthetic seawater. PC–PFA–MK concrete covering four different total cement replacement levels (10%, 20%, 30% and 40%) and with various MK:PFA proportions was exposed to synthetic seawater for up to 1.5 years. The chloride concentration–penetration depth profiles and change in compressive strength of the concrete for a range of binder compositions and at various exposure times are compared with those of the control PC concrete. It is established that blending the binders in PC concrete and PC–PFA concrete with MK produces concrete with a reduced strength deterioration factor (SDF) and good resistance to chloride penetration when exposed to seawater. The results presented in this paper form part of an investigation into the performance of concrete incorporating both PFA and MK in the binder to produce high performance concrete.

Keywords: Chloride ingress; Compressive strength; Metakaolin; Fly ash; Curing

1. Introduction

It is generally established that hydrated Portland cement (PC) in mortar and concrete is susceptible to attack by seawater, which contains both chloride and sulphate. The principal outcomes are a significant loss of strength, due primarily to decalcification of the C–S–H gel, and diffusion of chloride ions into the concrete, which can initiate corrosion of steel reinforcement. Partial replacement of PC by pozzolans can retard these processes. This paper deals with the influence of metakaolin (MK), pulverised fuel ash (PFA), and blends of MK and PFA on the durability of concrete exposed to seawater. Workability and strength data have been reported previously on these concretes [1,2]. There have been a number of reports of the effects of individual pozzolans on concrete durability during exposure to seawater or to chloride solutions, but not blends of the two pozzolans studied here.

Cabrera and Nwaubani [3] measured the effective chloride diffusion coefficients of PC, PC–15% PFA and PC–15% MK (for two different MKs) pastes using a chloride diffusion cell. The pastes of water/binder (w/b) ratio 0.4 were moist-cured (100% RH) for 60 days before being placed in the cell. Both the PC–MK and the PC–PFA pastes gave lower chloride diffusion coefficients than the PC paste, and the former gave particularly low values. Zhang and Malhotra [4] measured the resistance to chloride penetration of PC concrete and PC–10% MK concrete. The concrete of w/b ratio 0.4 was moist-cured for 28 and 91 days prior to being subjected to electrical conductivity measurements in compliance with the ASTM C1202 test. The PC–MK concrete showed significantly lower conductivity values than the PC concrete. In much more detailed studies, Thomas et al. [5] and Hooton et al. [6] determined the chloride penetration resistance of concrete of w/b ratios 0.3 and 0.4 containing 0%, 8% and 12% replacement of PC with ‘high-reactivity MK’ (HRM). Data were presented in the form of ‘apparent diffusion coefficients’ calculated using Fick’s second law of diffusion from chloride concentration–depth profiles after 28, 90 and 140 days exposure to 1.0 mol/l NaCl solution. Two more recent publications [7,8] extend these periods to 365 and 1095 days. The apparent diffusion coefficients were reduced on increasing the exposure time and on decreasing the w/b ratio and showed

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Table 1
Composition of PC, PFA and MK

Oxide	PC[a] (%)	PFA[b] (%)	MK[c] (%)
SiO_2	21.0	49.8	52.1
Al_2O_3	4.63	26.4	41.0
Fe_2O_3	2.26	9.3	4.32
CaO	65.6	1.4	0.07
MgO	1.18	1.4	0.19
SO_3	–	0.8	–
Na_2O	0.16	1.5	0.26
K_2O	0.78	3.5	0.63
TiO_2	–	1.0	0.81
Cl	0.01	0.01	–
LOI	0.99	4.9	0.6

[a] Data supplied by Rugby Cement.
[b] Data supplied by Ash Resources.
[c] Data supplied by Imerys (formerly ECC International).

marked decreases with increasing HRM content. In addition, the authors [5] determined the chloride binding capacity of cement paste with and without 8% HRM by exposing dried paste samples to various concentrations of NaCl solution and determining the amount of chloride removed from solution on establishment of equilibrium. For up to a 1-M solution concentration, the binding capacities of the two pastes were similar but above this concentration the binding capacity of the HRM paste increased at a much greater rate with increased solution concentration than did the pure PC paste. Coleman and Page [9] have also established, from analysis of the pore solutions of cement pastes made up with chloride containing water (2, 8 and 20 g/l) and cured for up to 101 days, that MK, when used as a partial cement replacement, produces a significant increase in chloride binding capacity of the paste. This is attributed to the reaction products formed from the pozzolanic reaction of MK with the calcium hydroxide (CH).

Leng et al. [10] have shown that the chloride ion diffusion coefficient of concrete (determined using the Nernst–Einstein equation) decreases with increasing replacement of PC with PFA. The decrease was attributed to changes in pore size distribution, increased C–S–H gel formation and increased alumina levels enabling more chloride to be fixed as Friedel's salt ($C_3A{\cdot}CaCl_2{\cdot}10\ H_2O$). Papadakis [11] has demonstrated that increasing cement replacement by FA in mortar exposed to NaCl solution produces (relative to the equivalent PC mortar) decreasing chloride concentrations. This applies at all depths in the mortar, except for a thin surface layer. The mortar was first water-cured for 1 year and then immersed in NaCl solution for 100 days, thus, the authors [11] did not study the effect of the exposure period on chloride penetration. The increased chloride concentrations in the surface layers, in mortars containing pozzolan, are attributed to the increased chloride binding capacity of these mortars. This is a result of the higher C–S–H content, which can bind Na^+ ions and their accompanying Cl^- ions, especially when the C–S–H has a reduced C/S ratio. Torii et al. [12] determined the apparent diffusion coefficients from chloride distribution profiles in PC concrete and concrete containing PC replaced with 30% PFA, at w/b ratios of 0.45, 0.55 and 0.65. After initial curing, the concrete was exposed to a sea shore and chloride concentration–depth profiles were determined after 8 months and 2 years exposure. For all the concretes, Friedel's salt and ettringite were present in the surface layers, and particularly for concretes containing mineral admixtures CH was absent in the surface region and was replaced with brucite and calcite. The mineral admixtures reduced the level of chloride penetration into the concrete and were much more effective in reducing chloride ingress than were reductions in w/c ratio in the PC concrete, particularly at long exposure periods. This suggests that chloride binding plays a dominant role in reducing the 'apparent' chloride diffusion coefficient.

Chloride diffusion measurements have also been carried out, on concrete made with ternary binders [13] involving PFA and silica fume (SF). The concrete employed PC, PC–8% SF, PC–25% PFA and PC–8% SF plus 25% PFA as binders and was cured for up to 2 years. Chloride diffusion coefficients were determined for concrete of various ages placed in a chloride diffusion cell. Relative to the PC concrete, at early ages, the SF concrete produced a sharp fall in diffusion coefficient followed by a gradual decline, whereas the PFA concrete showed a continuous and progressive reduction. In the ternary blend, the reduction in chloride diffusion coefficient was even greater in the early age concrete and continued to decline with concrete age more steeply than the SF concrete, suggesting that ternary blends should provide very high resistance to chloride penetration.

Both MK and PFA, when used as partial cement replacement, have been shown to reduce the strength retardation experienced by concrete or mortar exposed to seawater. Bosc et al. [14] produced mortar prisms with 0% and 30% replacement of PC with MK, moist-cured them for 28 days and immersed some in seawater and some in distilled water, some at 20 °C for 180 days and some at 30 °C for 90 days.

Table 2
Mix proportions, w/b = 0.5

%			Mix proportions, kg/m^3					
PC	PFA	MK	PC	PFA	MK	Sand	10-mm aggregate	20-mm aggregate
100	0	0	390.0	0.0	0.0	755.0	335.6	783.0
90	10	0	351.0	39.0	0.0	750.3	333.5	778.1
	7.5	2.5	351.0	29.3	9.8	750.6	333.6	778.3
	5	5	351.0	19.5	19.5	750.9	333.7	778.6
	2.5	7.5	351.0	9.8	29.3	751.1	333.8	778.9
80	15	5	312.0	58.5	19.5	746.1	331.6	773.7
70	30	0	273.0	117.0	0.0	740.8	329.2	768.2
	27.5	2.5	273.0	107.3	9.8	741.1	329.4	768.5
	25	5	273.0	97.5	19.5	741.4	329.5	768.8
	22.5	7.5	273.0	87.8	29.3	741.6	329.6	769.1
60	30	10	234.0	117.0	39.0	737.2	327.6	764.4

Mass of water = 195 kg/m^3.

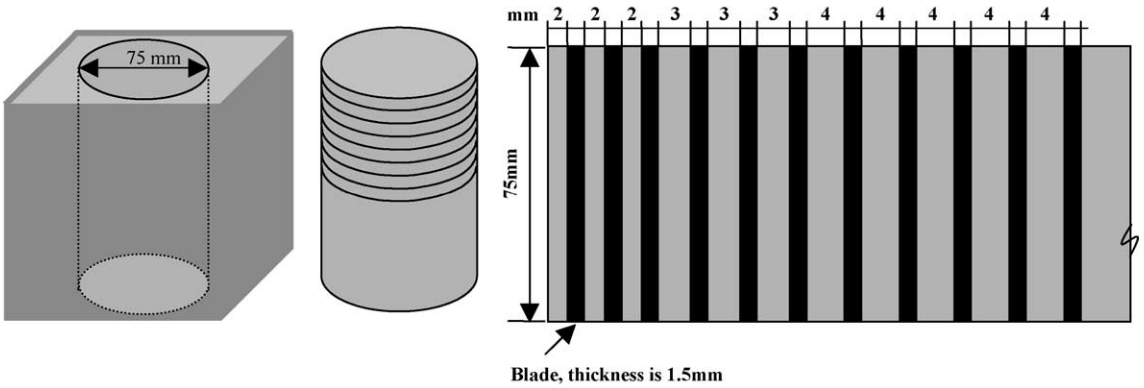

Fig. 1. Sample slices for chloride ingress profile measurement.

Relative to water-cured mortar, the seawater-exposed specimens showed reduced strength, but the retardation in strength was much less for the MK mortars. This was attributed to increased pore refinement and reduced permeability for these mortars. Kumar [15] investigated the percentage loss in strength (strength deterioration factor or SDF) of marine exposed concrete relative to equivalent water-cured concrete for concretes prepared with 0%, 10%, 20% and 30% PFA replacing types I, II and V PC binders. After 1 year of exposure, concretes with PC replacements of up to 20% PFA for types I and II cement resulted in much lower SDFs. This was not the case with type V cement, even though type V cement has a much lower C_3A content (1.9%) than type I (9.5%) cement, and hence a lower chloride binding capacity. This indicates that in a marine environment type I cement blended with pozzolan will produce more durable concrete than type V cement.

Reports in the literature on determination of chloride diffusion coefficients and on chloride penetration [3,16] suggest that measurement of chloride diffusion coefficients to predict chloride penetration in concrete exposed to

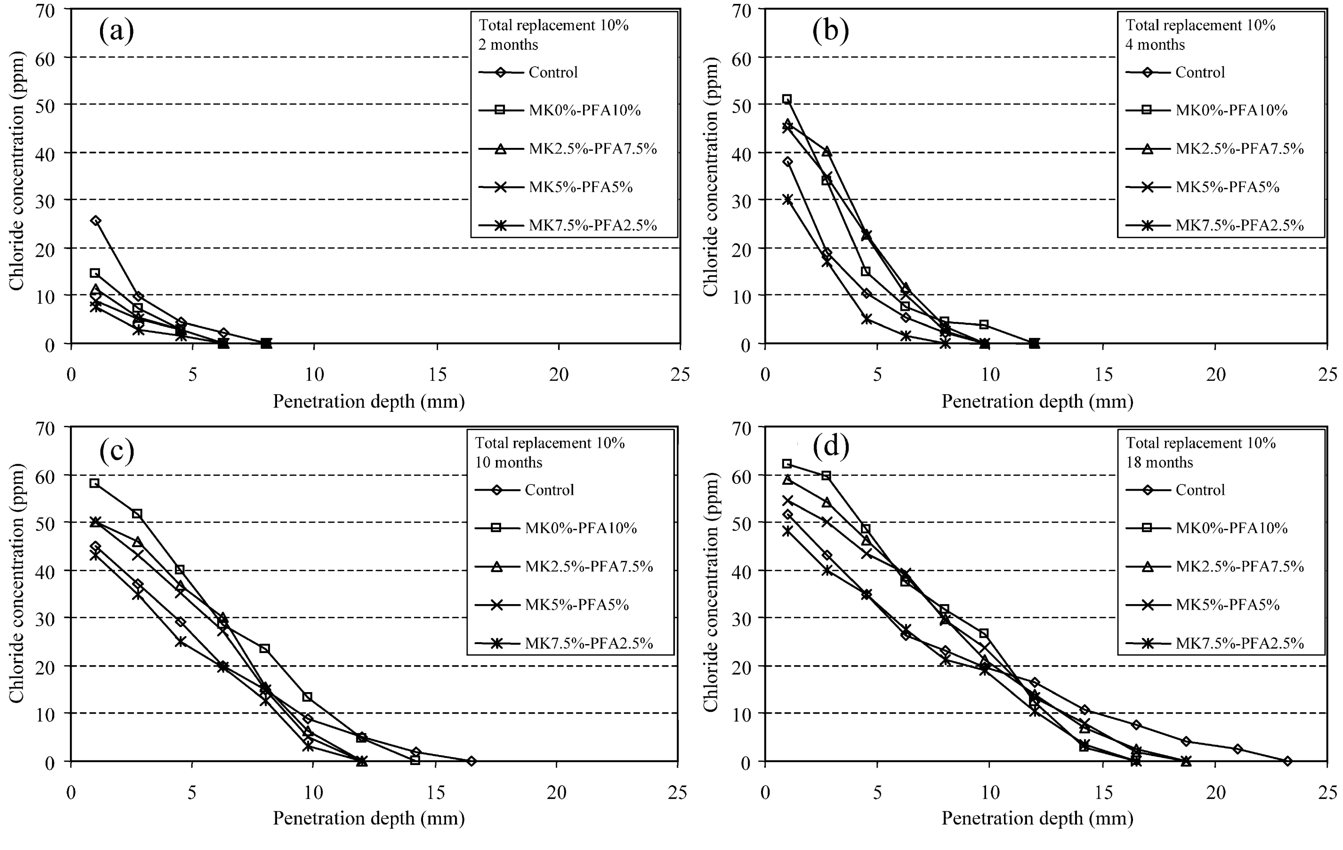

Fig. 2. Chloride concentration ingress profile with depth for 2, 4, 10 and 18 months at 10% cement replacement.

chloride sources can be misleading. This is because the hydrating concrete binder comprises a dynamic system in which the diffusion coefficient will change with time because of the continued formation of hydration products, which leads to pore refinement and pore blocking [7,16,17]. Also, the calculated chloride diffusivities are in practice 'apparent' diffusivities and do not take account of the effect that chemical binding has on the transport of chloride ions. Therefore, it is difficult to predict the rate and level of chloride penetration with time from measured chloride diffusion coefficients employing chloride diffusion cells, and it is much more realistic to measure chloride penetration–depth profiles under the intended exposure conditions. The current paper reports the results of such measurements on concrete produced with PC–MK, PC–PFA and PC–PFA–MK binders exposed to synthetic seawater for up to 1.5 years. It also reports the strength retardation of the different concretes resulting from seawater exposure.

2. Experimental details

2.1. Materials and mixtures

PC in compliance with BS 12:1996 [18] was used throughout the investigation. Ash Resources supplied the PFA, and the MK was supplied by Imerys (formerly ECC International). The compositions of the three binder constituents are given in Table 1. Natural sea dredged sand of grading M–F complying with BS 882:1992 [19] was used throughout the investigation. The coarse aggregates employed were 10- and 20-mm crushed limestone.

Eleven mixes, with a binder (PC–PFA–MK) content of 390 kg/m^3, w/b ratio of 0.5 and a wide range of MK–PFA combinations, were investigated. In addition to PC only (control) mixtures, total cement replacement levels (MK and PFA) of 10%, 20%, 30% and 40% by mass were studied. From cost-effectiveness considerations, the proportion of MK did not exceed that of PFA, other than for the lowest cement replacement level (10%). Workabilities were in the range 35–130 mm. The compositions of the binder components and mixture details for the concretes of this study are given in Table 2. No chemical admixtures were used.

2.2. Sample preparation and curing

The sampling was carried out in accordance with BS 1881-108:1983 [20]. Each 100-mm cube mould was filled with concrete, vibrated to give good compaction and covered with cling film for 24 h to preserve the initial moisture condition of the sample. The cubes were de-moulded and water-cured for 28 days followed by exposure to synthetic

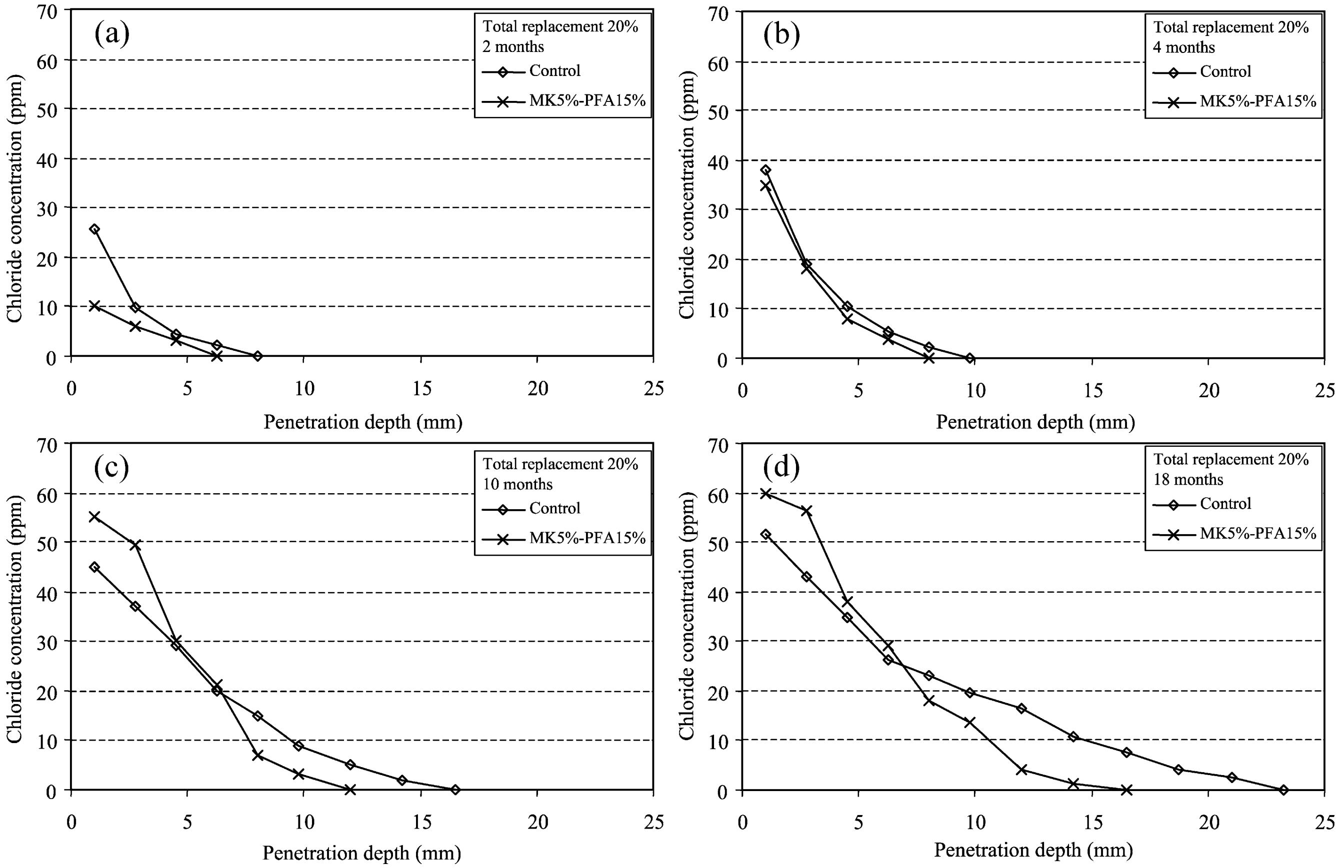

Fig. 3. Chloride concentration ingress profile with depth for 2, 4, 10 and 18 months at 20% cement replacement.

seawater [21] for up to 18 months at 20 ± 2 °C. The cubes used for producing chloride test specimens were coated with Poxtar F (a two-part hardener and resin coating material resistant to submersion in seawater with high chemical resistance for concrete) on four adjacent faces, including the top trowelled face, leaving two opposite uncoated faces exposed to either water or synthetic seawater. The composition of the synthetic seawater was 30 g/l NaCl, 6 g/l $MgCl_2$, 5 g/l $MgSO_4$, 1.5 g/l $CaSO_4 \cdot 2H_2O$ and 0.2 g/l $KHCO_3$. The chloride test specimens comprised 75-mm diameter slices of different thicknesses dry-cut from the surface to the centre of cylindrical cores. These were obtained by coring along the line joining the centres of the two uncoated surfaces of the concrete cubes (see Fig. 1). The concrete slices obtained were then dried at 105 °C to constant mass and ground into fine powders (< 150 μm) for chemical analysis.

2.3. Test procedures

Strength tests were carried out at each of the water and synthetic seawater curing times of 28 days, 2, 4, 10 and 18 months. The compressive strength values were determined from the average of two cube tests carried out in accordance with BS 1881-116 [22].

In parallel with the strength tests, chloride tests were carried out to measure the chloride ingress profile. Samples (powders) of 5 g obtained during the sample preparation stage were dissolved in 10% (w/w) HNO_3 solution, boiled on a hotplate for 10 min, simmered for a further 15 min and then left to cool. The cooled samples were filtered under vacuum through a quantitative grade filter paper, the residue being washed with boiling deionised water. Filtrate and washings were made up to 500 ml with deionised water. A 50-ml sample of filtrate together with 5 ml of buffer was finally analysed using a pH/ion meter (Model 225 pH/Ion meter) and standard solutions for calibration and reference, to obtain the chloride concentration (ppm). Each reading is taken as the average chloride concentration of the measured slice at half its thickness. The base chloride concentration (i.e., that in the original mix components) was found to be negligible and therefore no correction to the data was necessary. Chloride concentrations are quoted in terms of ppm by mass of concrete.

3. Results

The chloride concentration–penetration depth profiles for the selected concretes (which were exposed to synthetic seawater for 2, 4, 10 and 18 months) are presented in Figs. 2–5, for cement replacement levels of 10%, 20%, 30% and 40%, respectively. Table 3 gives an example of chloride

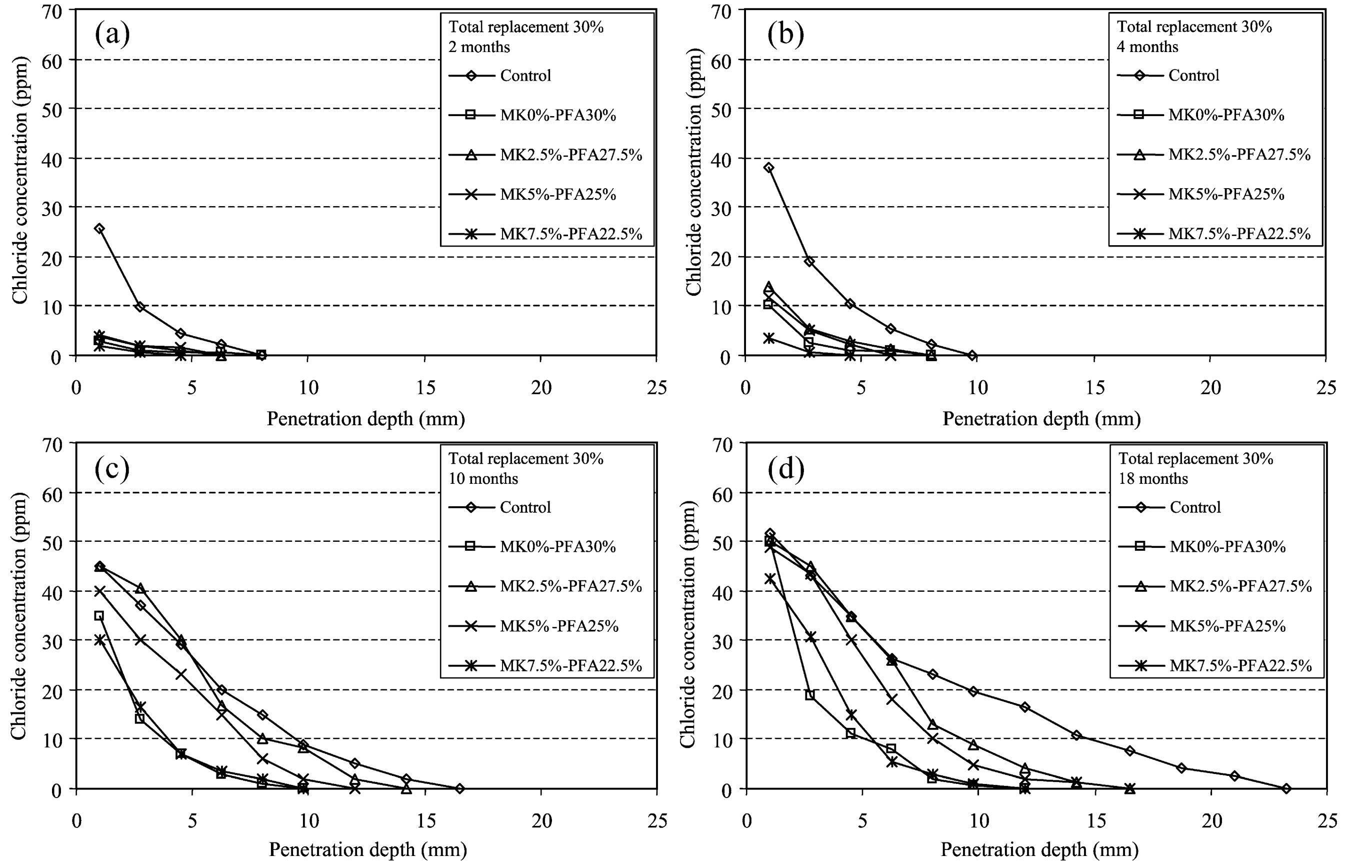

Fig. 4. Chloride concentration ingress profile with depth for 2, 4, 10 and 18 months at 30% cement replacement.

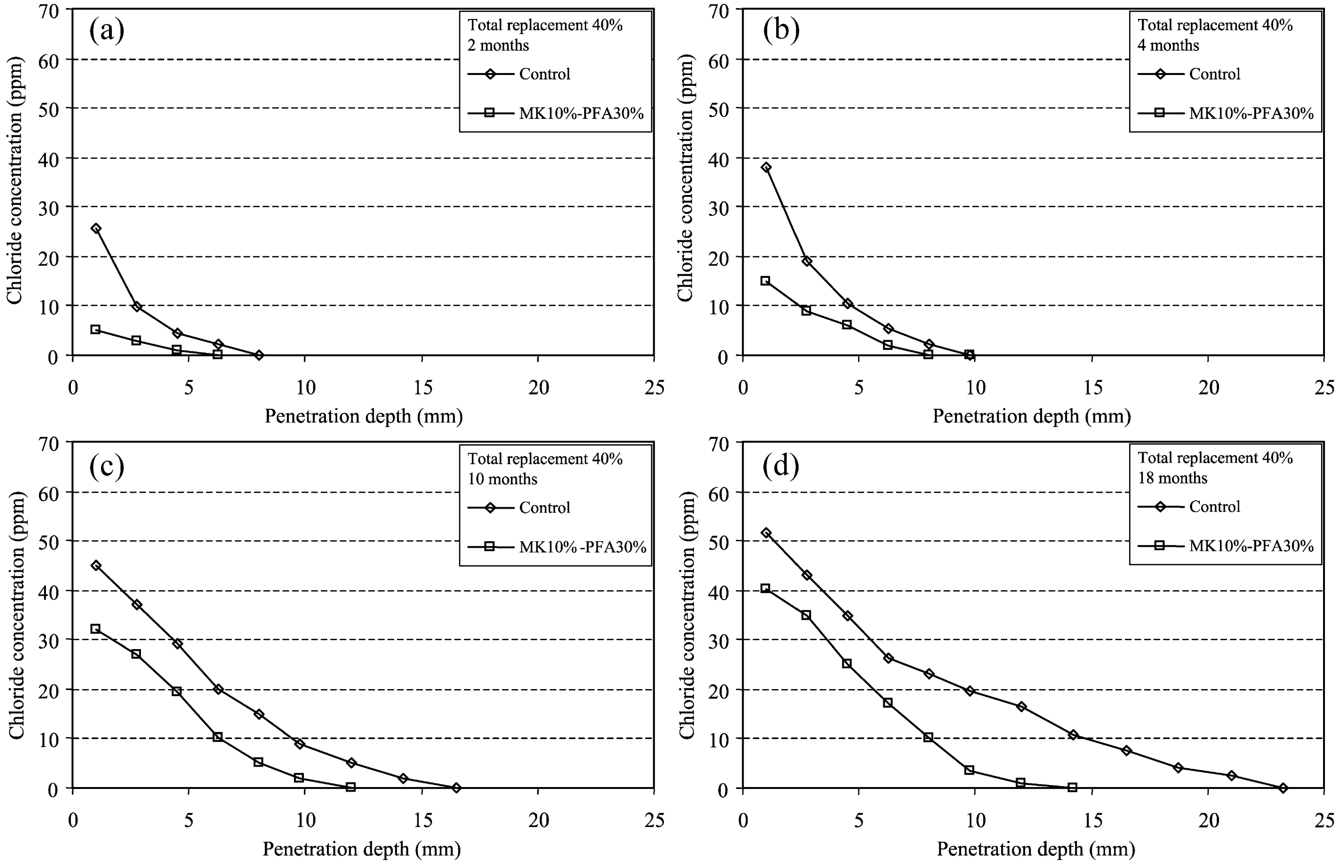

Fig. 5. Chloride concentration ingress profile with depth for 2, 4, 10 and 18 months at 40% cement replacement.

concentration–penetration depth data for 30% total replacement. At all four total cement replacement levels, it was found that for concrete made with blended binders, the chloride concentration–penetration depth profiles become steeper with increase in exposure time, whereas for the control concrete (with PC binder) the chloride concentration–penetration depth profiles become shallower with increase in exposure time. The steepening of the 'profile'

Table 3
An example of chloride concentration (ppm)–penetration depth (mm) data for 30% total replacement

Mixes	Depth, mm											
	1	2.75	4.5	6.25	8	9.75	12	14.3	16.5	18.8	21	23.3
2 months												
Control	25.5	9.8	4.5	2.1	0	–	–	–	–	–	–	–
0% MK–30% PFA	3	1	0.77	0.72	0	–	–	–	–	–	–	–
7.5% MK–22.5% PFA	2	0.5	0	–	–	–	–	–	–	–	–	–
4 months												
Control	38	19	10.5	5.5	2.3	0	–	–	–	–	–	–
0% MK–30% PFA	10	2.5	1	0.8	0	–	–	–	–	–	–	–
7.5% MK–22.5% PFA	3.5	0.67	0	–	–	–	–	–	–	–	–	–
10 months												
Control	45	37	29	20	15	9	5	2	0	–	–	–
0% MK–30% PFA	35	14	7	2.93	1	0	–	–	–	–	–	–
7.5% MK–22.5% PFA	30	16.6	7	3.36	2	0	–	–	–	–	–	–
18 months												
Control	51.7	43	35	26.4	23	19.5	16.5	10.8	7.6	4	2.5	0
0% MK–30% PFA	50.1	18.7	11	7.86	2	0.78	0	–	–	–	–	–
7.5% MK–22.5% PFA	42.5	30.6	15	5.48	3	1	0	–	–	–	–	–

is particularly pronounced for concrete made with PC–PFA binary binders (compare Fig. 2a with Fig. 2d and Fig. 4a with Fig. 4d). This contrasting behaviour occurs both because the chloride concentrations in the outer region (1–5 mm) of pozzolan-containing concrete increase more rapidly with increase in exposure time than do those for the control concrete, and the depth to which chloride penetrates with time increases more rapidly for the control concrete than for the pozzolan-containing concrete. The effect is attributed to the relative changes in intrinsic diffusivity and chloride binding capacity with age exhibited by the different binder compositions.

For concrete containing ternary blended binders, MK has a significant influence on both chloride concentration and penetration depth. At short exposure times (2 and 4 months), increasing MK contents result generally in lower chloride concentrations and reduced penetration depths (Figs. 2a,b and 5a,b). However, at long exposure times (18 months), the trend is less clear as both the concrete containing binary PC–PFA binders, together with the concrete containing ternary PC–PFA–MK binders with the highest MK levels, exhibit the lowest chloride penetration depths (Figs. 2d and 5d). Also, as the cement replacement level increases, there is a very marked reduction in the chloride ion concentration levels particularly within the first 10 mm of concrete and, in addition, the total penetration depth is reduced.

Fig. 6 shows the change in compressive strength with age at four different total cement replacement levels (10%, 20%, 30% and 40%) for PC–PFA–MK concrete with various MK:PFA proportions, water-cured for up to 18 months. In each case, strengths are compared with the control (PC only) concrete and the equivalent PC–PFA concrete. MK enhances substantially the early (28 days) strength, whereas PFA retards early strength. The degree of early strength enhancement (due to MK) or retardation (due to PFA) is in direct relation to the amount of MK or PFA present. At long curing periods (18 months), both MK and PFA enhance strength and the difference in strengths achieved with the different blend proportions at 10% and 30% total replacement (Fig. 6a and c) is relatively small. In fact, the PC–PFA blend concrete performs as well or slightly better than the PC–PFA–MK blend concrete.

Fig. 7 shows the change in compressive strength with age of these concretes cured in water for 28 days and then

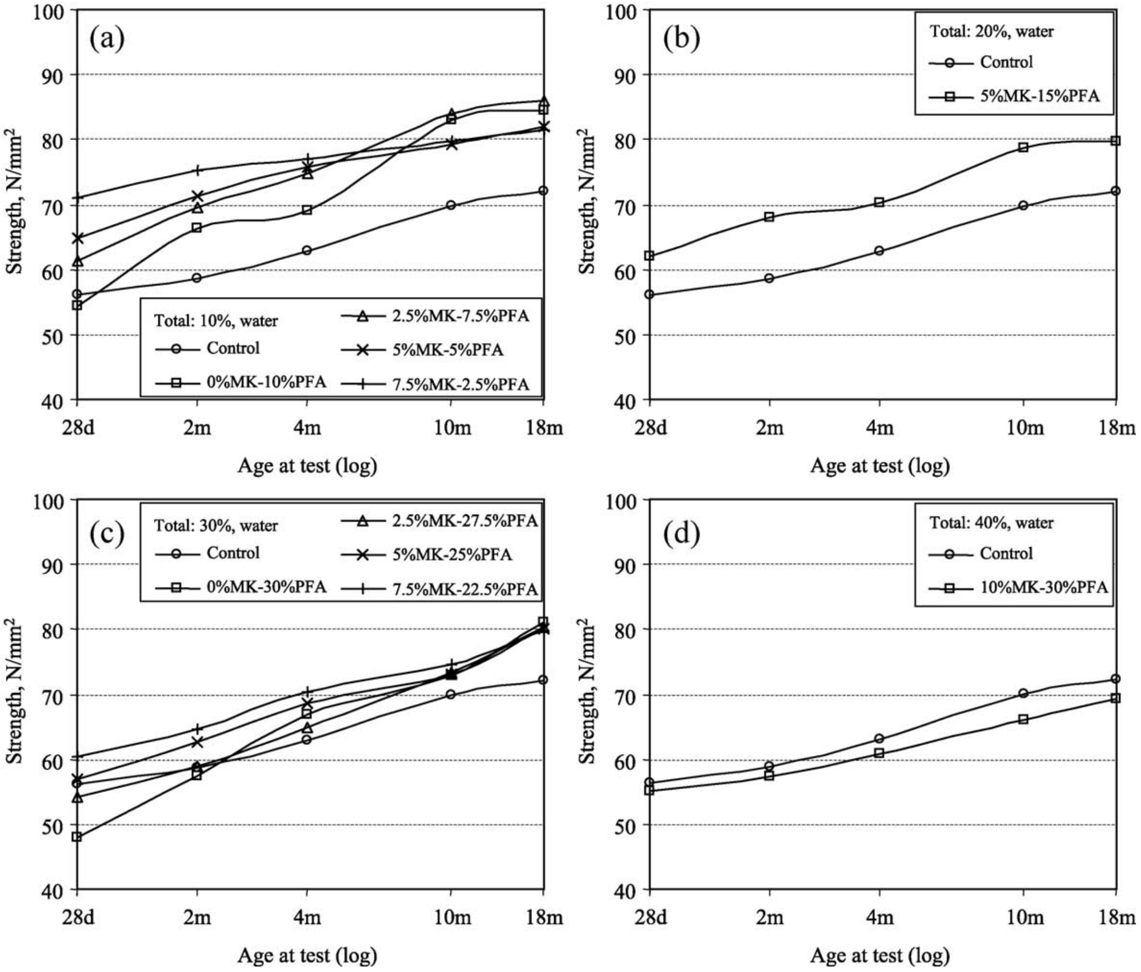

Fig. 6. Compressive strength with age at 10%, 20%, 30% and 40% cement replacements for water-cured concrete.

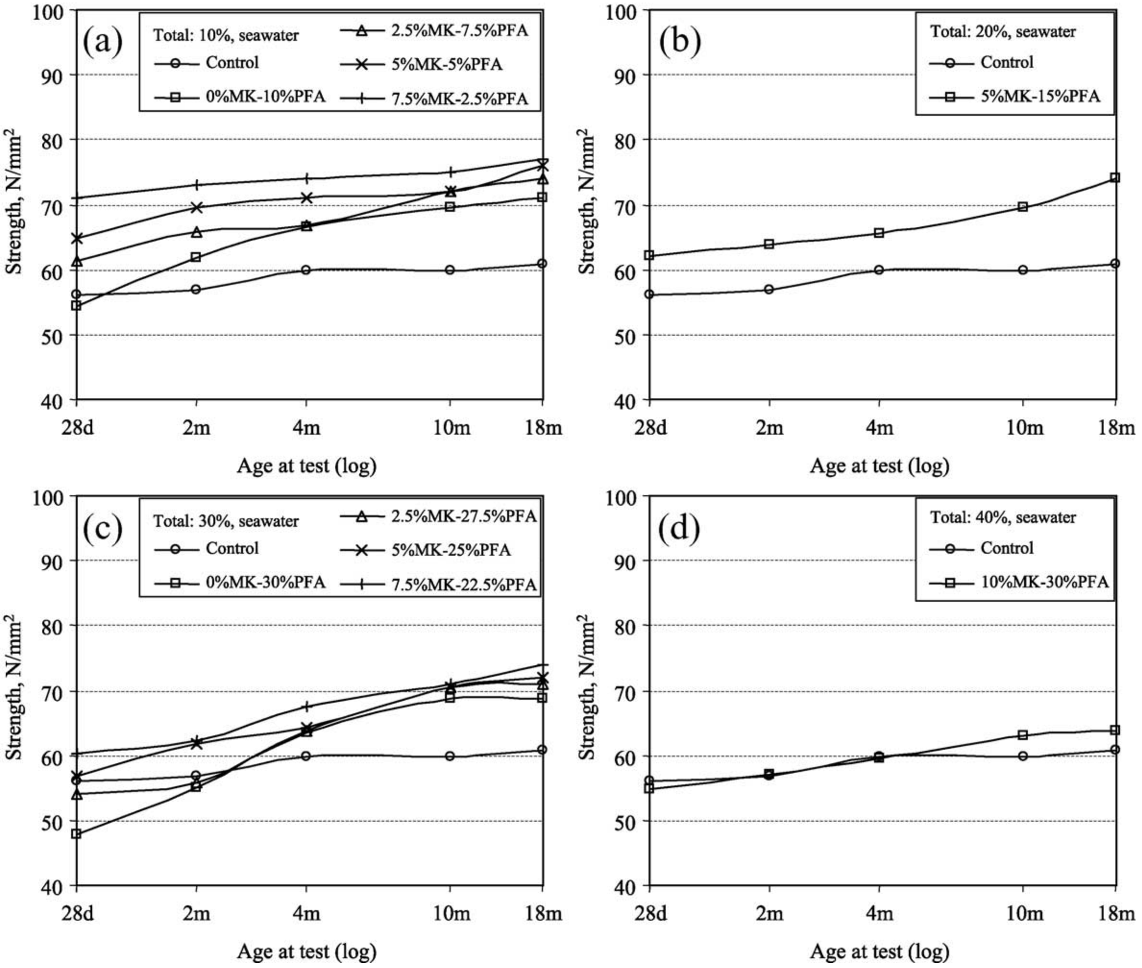

Fig. 7. Compressive strength with age at 10%, 20%, 30% and 40% cement replacements for seawater-cured concrete.

exposed to synthetic seawater up to an age of 18 months. Note that time-zero is from de-moulding. The strength development of the selected concretes in seawater (after an initial 28 days water curing) relative to equivalent water-cured concrete is clearly retarded, with long-term strengths being reduced by between 5.5% and 16% depending on the binder composition. In particular, PC concrete shows no gain in strength beyond 4 months in seawater relative to its strength in water. The PC–PFA concrete also shows greatly retarded strength development after 4 months. At all total cement replacement levels, the advantage of employing PC–PFA–MK blends instead of equivalent PC–PFA blends is clearly apparent. Ternary blends reduce the strength retardation in seawater relative to the strength retardation in seawater of equivalent concrete made with PC binder or PC–PFA binder. Although when water-cured for long periods (18 months), the PC–PFA concrete at 10% replacement performs better than the PC–PFA–MK concrete, when exposed to seawater the PC–PFA–MK concrete performs significantly better than the PC–PFA concrete (Fig. 7). This improved performance after 18 months in seawater by the ternary blend concretes, with PC replacement levels up to 40%, is very evident when the 'SDFs' are calculated (see Fig. 8). As the proportion of the MK pozzolan increases, the SDF decreases.

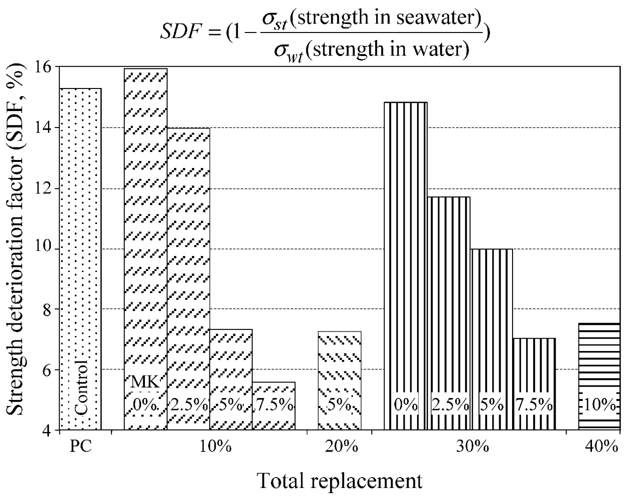

Fig. 8. Strength deteriorate factor at 10%, 20%, 30% and 40% cement replacements for 18 months curing.

4. Discussion

Chlorides in concrete can be either dissolved in the pore solution as free chlorides or chemically combined with and physically bound to the cementitious reaction products as bound chlorides [16]. The capacity of cementitious compounds to bind chloride ions reduces substantially the rate of chloride ion transport in concrete by an amount related to the binding capacity of the binder. Also, the binding capacity increases with increase in chloride concentration in solution, thus, as chloride diffuses into the concrete via the pore solution, the binding capacity of the cement hydrates will also increase. Initially, the surface, which on immersion is immediately in contact with the seawater, will show a high level of bound chlorides (and total chlorides). Also, this level would be expected to decrease in concrete with PC–PFA–MK binders as the PC replacement level increases, because of the initially reduced binding capacity of the paste, which is diluted with pozzolan (Figs. 2a–5a). However, with increase in exposure time, due to the continuing pozzolanic reaction and the formation of additional hydrate products, the binding capacity of the PC–PFA–MK pastes will increase more rapidly than the PC paste. Thus, the chloride concentrations in the surface layers of the PC–PFA–MK concretes will approach or exceed that in the PC concrete (Figs. 2d–5d). The results also suggest that the binding capacity of the reaction products deriving from PFA is greater than from the MK reaction products (compare Figs. 2d and 4d). Thus, at very high replacement levels, and particularly for those binders containing high proportions of MK, the increase in binding capacity of the products deriving from the pozzolanic reaction may not compensate for that lost due to the reduced PC content (Figs. 4d and 5d).

Due to the formation of the pozzolanic reaction products within the capillary pore spaces, in addition to an increase in the binding capacity of the paste, the pore system will also become finer and more segmented. Thus, the effective chloride diffusivity will drop sharply with increased exposure time severely limiting the penetration of chloride ions for PC–PFA–MK concrete relative to PC concrete (compare Fig. 2a with Fig. 2d, Fig. 3a with Fig. 3d, Fig. 4a with Fig. 4d and Fig. 5a with Fig. 5d). Therefore, relative to the PC concrete, the chloride concentration–depth profiles will become much steeper with increase in curing period, and relative to the PC concrete the maximum penetration depth will diminish (Figs. 2–5). The results indicate that PFA has a greater influence on binding capacity (and its associated effect on depressing chloride diffusivity) than has MK. However, mercury porosimetry work on these compositions by the authors (to be published in a further paper) shows that increasing the proportion of MK in PC–PFA–MK pastes produces a finer pore structure, which will also depress the effective chloride diffusivity. Thus, the relationship between blend composition and total chloride penetration is complex. From the current results, it would appear that either PC–PFA concrete or PC–PFA–MK concrete with MK levels of 7.5% and above will result in the lowest chloride penetration, and PC–PFA–MK concrete with smaller MK levels will give higher levels of penetration, although still much smaller than those for PC concrete.

With respect to strength retardation in seawater relative to water concrete made with the binary PC–PFA blends and with the ternary PC–PFA–MK blends, both exhibit reduced strength deterioration factors relative to PC concrete. Also, increasing the proportion of MK in the PC–PFA–MK concrete produces further improvement in durability. This is attributed to development of a finer pore structure as the MK content increases, which reduces the rate of diffusion of aggressive species into the concrete.

5. Conclusions

- Significant reductions in chloride penetration depths occur when PC is partially replaced with PFA and MK. These reductions increase with both increasing total replacement level and increasing exposure time. This is attributed to the relative changes in intrinsic diffusivity and chloride binding capacity with age exhibited by the different binder compositions.
- In ternary PC–PFA–MK blends, MK has a significant beneficial effect on both the chloride concentration and penetration depth. At short exposure duration (2 and 4 months) increasing MK content generally leads to reduced concentration and penetration depth.
- A 30% PC replacement by PFA is particularly effective in decreasing both the chloride concentration and penetration depth, especially at long exposure times.
- In the case of binary blends, substantial enhancement with MK and reduction with PFA in early compressive strength (28 days) of the water-cured specimens occurs. At long curing times (18 months) both MK and PFA enhance strength.
- Both binary (PC–PFA) and ternary blends cause significant improvement in compressive strength of concrete exposed to seawater compared to that of the control concrete. The strength retardation in seawater exposed specimens is significantly reduced when the control and PC–PFA concrete is further blended with MK.

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