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EFFECT OF CEMENT TYPE ON CHLORIDE BINDING AND CORROSION OF STEEL IN CONCRETE

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ABSTRACT

Chloride binding and its influence on the rate of reinforcement corrosion has been investigated in a range of mixes by, respectively, pore solution analysis and measuring the galvanic current in macro corrosion cells formed by embedding mild steel bars in two layers of concrete. For chloride derived from NaCl and introduced at the time of mixing, chloride binding occurred in the order of: GGBS>PFA>OPC>SF and the amount of unbound (ie free) chloride increased with increasing chloride content. However the corrosion rates occurred in the order of PFA>SF>GGBS>OPC at 1% Cl^- and PFA>OPC>GGBS>SF at 3% Cl^-. The corrosion rates increased with increasing chloride content for all mixes due to an increase in the amount of free chloride. The higher rates of corrosion for PFA (and GGBS at 1% Cl^-) compared with OPC was attributable to a reduction in the OH concentration as a result of the pozzolanic reaction. The relatively low rate of corrosion for SF at 3% Cl^- is thought to largely depend upon the physical characteristics of the matrix rather than the pore solution chemistry.

Introduction

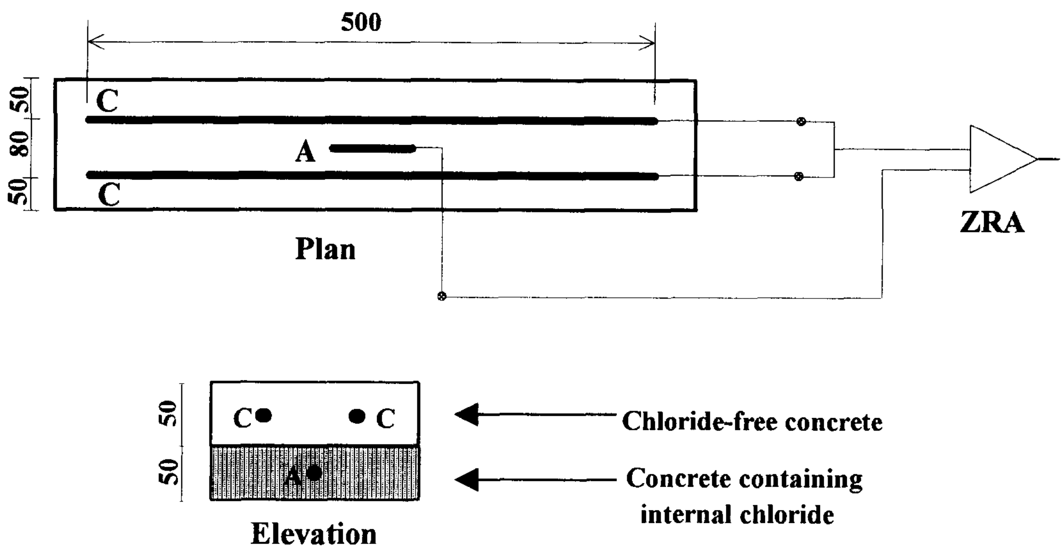
Chlorides are the principal cause of reinforcement corrosion in concrete structures. If the concentration of chlorides exceed a threshold value, the passive oxide film on the surface of the reinforcement is disrupted. In the presence of oxygen and moisture corrosion then occurs.

The chlorides may be introduced at the time of mixing (internal chloride) or penetrate once the concrete has hardened (external chloride). With internal chloride the amount of chloride which can become physically and/or chemically bound with the cement hydrates depends upon, principally, the cementitious material and the total chloride content [1]. Since it is believed that it is the chloride remaining in solution (i.e. free chloride) that influences reinforcement corrosion [2], concretes which bind high proportions of chlorides should offer greater protection to embedded steel from the risk of corrosion.

This paper reports on an investigation into the relationship between chloride binding and reinforcement corrosion using cement pastes and concretes with internal chloride derived from sodium chloride. The chloride binding capacity was estimated by expressing pore solution from cement paste specimens. The influence of the aggregate on chloride binding was ignored. Corrosion of steel in concrete was investigated by measuring the galvanic current in macro corrosion cells, the construction details of which are given below.

Corrosion cell

Fig. 1 shows the corrosion cell used in this work [3]. The corrosion cell consists of two 50mm thick layers of concrete containing embedded mild steel electrodes placed 25mm and 75mm above the base. The mix in the lower layer is dosed with chlorides. Once it has hardened the upper, chloride free, layer is poured.



A Mild Steel Anode 8mm diameter 50mm long
C Mild Steel Cathodes 8mm diameter 500mm long
All dimensions in mm

FIG. 1
Corrosion cell

The lower layer contains a mild steel electrode 8mm diameter 50mm long which acts as an anode (Fig. 2). The top layer contains two mild steel electrodes 8mm diameter 500mm long which act as cathodes. The electrodes are held in position using 3mm diameter mild steel wire which is attached to the electrode via push connections. Prior to concreting, the exposed ends of the wire are coated in a polymer modified cementitious grout and covered in heat shrink sleeving in order to minimise the risk of crevice corrosion. The galvanic current flowing in the cell is measured by means of a zero resistance ammeter [4].

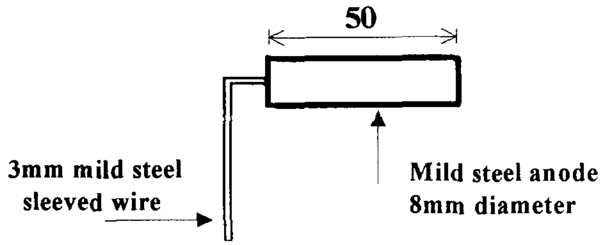


FIG. 2
Anode

Experimental procedure

(i) Chloride binding

Mix details of the cement pastes used for pore pressing are given in Table 1. The composition of the cement and extenders used in this work are given in Table 2.

TABLE 1
Mix details (pore press)

Mix Ref	w/c	OPC	GGBS	PFA	SF	Total Cl^{-*} (%)	Hydration time (days)
1	0.5	1.00	-	-	-	1.0	3,7,14,28,90,180
2	0.5	0.35	0.65	-	-	1.0	3,7,14,28,90,180
3	0.5	0.65	-	0.35	-	1.0	3,7,14,28,90,180
4	0.5	0.90	-	-	0.10	1.0	28,180
5	0.5	1.00	-	-	-	0.2	28
6	0.5	1.00	-	-	-	0.3	28
7	0.5	1.00	-	-	-	0.4	28
8	0.5	1.00	-	-	-	0.7	28
9	0.5	1.00	-	-	-	1.5	28
10	0.5	1.00	-	-	-	2.5	28
11	0.5	0.35	0.65	-	-	0.2	28
12	0.5	0.35	0.65	-	-	0.3	28
13	0.5	0.35	0.65	-	-	0.4	28
14	0.5	0.35	0.65	-	-	0.7	28
15	0.5	0.35	0.65	-	-	1.5	28
16	0.5	0.35	0.65	-	-	2.5	28
17	0.5	0.65	-	0.35	-	0.2	28
18	0.5	0.65	-	0.35	-	0.3	28
19	0.5	0.65	-	0.35	-	0.4	28
20	0.5	0.65	-	0.35	-	0.7	28
21	0.5	0.65	-	0.35	-	1.5	28
22	0.5	0.65	-	0.35	-	2.5	28

* Cl^- (% by weight of cement) derived from NaCl

TABLE 2
Composition of OPC, GGBS, PFA and SF (% by weight)

	OPC	PFA	GGBS	SF
CaO	65.4	3.9	41.6	0.3
SiO_2	20.9	51.1	35.0	92
Al_2O_3	4.9	26.3	11.6	1.0
Fe_2O_3	3.2	12.5	1.17	1.0
MgO	1.0	1.6	8.58	0.6
Mn_2O_3	*	*	0.32	*
TiO_2	*	0.9	0.54	*
Na_2O	0.14	0.8	0.27	0.1 - 0.4
K_2O	0.60	2.7	0.31	0.2 - 0.7
SO_3	2.7	0.70	*	0.3
S_2	*	--	*	*
C	*	--	*	1.5
Free CaO	0.8	--	*	*
Ignition loss	1.2	3.1	-1.28	*
Specific surface area (m^2/kg)	360	*	412	15000-20000

* not measured

Batches consisting of 9 kg and 1.5 kg of mixes 1-4 and 5-22 respectively, were prepared. The chloride ions were introduced into the mix by dissolving appropriate quantities of NaCl in the mix water. After thorough mixing, two replicates were cast in 45mm diameter 58mm long cylindrical pvc moulds and compacted by vibration. The moulds were sealed and rotated at 6 revs per minute for 24 hours to minimise segregation. Thereafter the specimens were stored in a sealed condition at 20 ± 1 °C.

At the end of the conditioning period, each set of two replicates was demoulded and the pore solution was expressed using a pore press [5]. Each specimen was subject to a maximum load of 900 kN, applied at a loading rate of 60 kN per minute. A measured volume of the expressed solution was diluted and analysed for Cl^- and OH^- ion concentrations. The Cl^- concentration was determined by potentiometric titration with silver nitrate solution using a chloride ion selective electrode [6]. The OH^- concentration was determined by titrating with 0.1M hydrochloric acid using phenolphthalein indicator.

(ii) Rate of corrosion

The mix proportions of the concretes used in the corrosion cells are shown in Table 3. Eight corrosion cells (A1, A3, B1, B3, C1, C3, D1 and D3) were tested. Corrosion cell A1 was made from mix A but with the lower 50mm layer of concrete dosed with 1% Cl^- (by weight of cement). Corrosion cell A3 was also made from mix A but with the lower 50mm layer of concrete dosed with 3% Cl^- (by weight of cement) (Fig. 3). Corrosion cells B1 and B3, C1 and C3 and D1 and D3 were similarly constructed using, respectively, mixes B, C and D.

A1 A3

FIG. 3
Composition of corrosion cells A1 and A3

The electrodes in the corrosion cells were connected immediately after the top layer of concrete was placed. The corrosion cells were removed from the moulds within 24 hours of casting and stored in a curing room at a temperature of 20±1 °C and 95±2% relative humidity for the duration of the test. The zero resistance ammeter readings were automatically logged, initially every 4 hours for the first week, then daily for the next three weeks and weekly thereafter. Three replicates of corrosion cells A1, B1, C1 and D1 and two replicates of cells A3, B3, C3 and D3 were tested.

TABLE 3
Mix proportions (corrosion cells)

	Mix A	Mix B	Mix C	Mix D
OPC	1.00	0.35	0.65	0.90
GGBS	--	0.65	--	--
PFA	--	--	0.35	--
SF	--	--	--	0.10
Sand	1.51	1.51	1.51	1.51
Aggregate (10mm)	0.69	0.69	0.69	0.69
Aggregate (20mm)	1.64	1.64	1.64	1.64
water/cement	0.5	0.5	0.5	0.5

Results and discussion

(i) Pore solution analyses

The results of the pore solution analyses of cement pastes containing 1% Cl^- (by weight of cement) (Mix Ref: 1-4) are shown in Figs. 4 and 5 respectively. The chloride concentration of the pore solution at zero days hydration was taken to be the same as the mix water.

Generally it can be seen that the majority of changes in chloride concentration take place during the first 28 days, particularly with mixes containing ground granulated blastfurnace slag (GGBS), pulverized fuel ash (PFA) and silica fume (SF). However, the hydroxyl concentrations stabilise at around 90 days.

Fig 4 also shows that GGBS (Mix 2) contains the lowest chloride concentration and silica fume (Mix 4) the highest, whereas Fig 5 shows that (ordinary Portland cement) OPC (Mix 1) has the highest

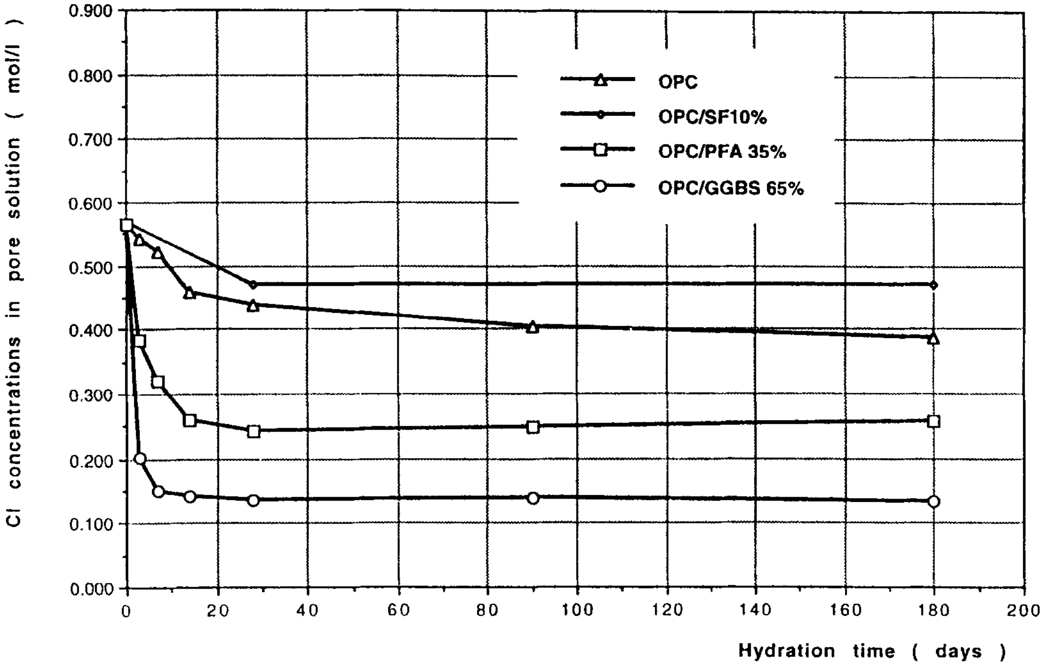


FIG. 4
Pore solution Cl^- concentration vs. hydration time for cement pastes with w/c=0.5 containing 1% internal Cl^- from NaCl

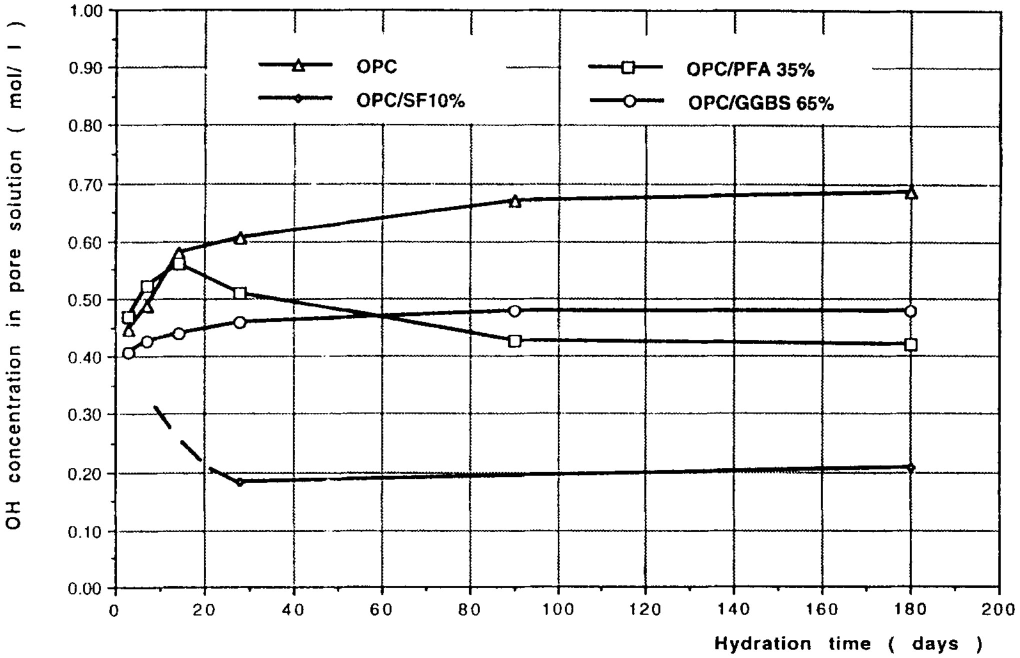


FIG. 5
Pore solution OH^- concentration vs. hydration time for cement pastes with w/c=0.5 containing 1% internal chloride from NaCl

hydroxyl ion concentration and silica fume the lowest. This suggests that concretes made with silica fume may have a low threshold for corrosion initiation (see below).

Figs 6 and 7 show how the chloride and hydroxyl ion concentrations in the pore solution vary with the total chloride content. For all cement types, the chloride concentration in the pore solution increased sharply with total chloride content. However, the hydroxyl ion concentrations were relatively unaffected. For instance with GGBS, the OH^- and Cl^- concentrations increased by 18% and 700% respectively as the dosage of chloride increased from 1% Cl^- to 2.5% Cl^- (by weight of cement). Fig 7 also shows that with pastes made from PFA and OPC alone, the OH^- concentration reduced over the same range of chloride additions.

(ii) Corrosion tests

The anodic current densities of corrosion cells A1, B1, C1 and D1 (dosed with 1% Cl^-) and corrosion cells A3, B3, C3 and D3 (dosed with 3% Cl^-) are shown in Figs 8 and 9 respectively.

At early ages the current densities increased sharply, presumably due to the fact that a large percentage of the chloride was still in solution and to the raised temperature occurring during hydration. However, beyond about 3 days the current densities gradually reduced and, in the case of corrosion cells A3, B3, C3 and D3 (Fig. 9), finally appeared to stabilise at approximately 90 days. This was presumably attributable to the fact that the majority of changes in the pore solution were completed by then (Figs 4 and 5). However, the current densities did fluctuate with time presumably due to small changes in the storage temperature and relative humidity.

Mixes with 1% Cl^- experienced far lower rates of corrosion than corresponding mixes dosed with 3% Cl^-. The results in Figs 6 and 7 suggest that this is probably due to significant differences in the % of free chloride in the two sets of mixes rather than differences in the OH^- concentration. This

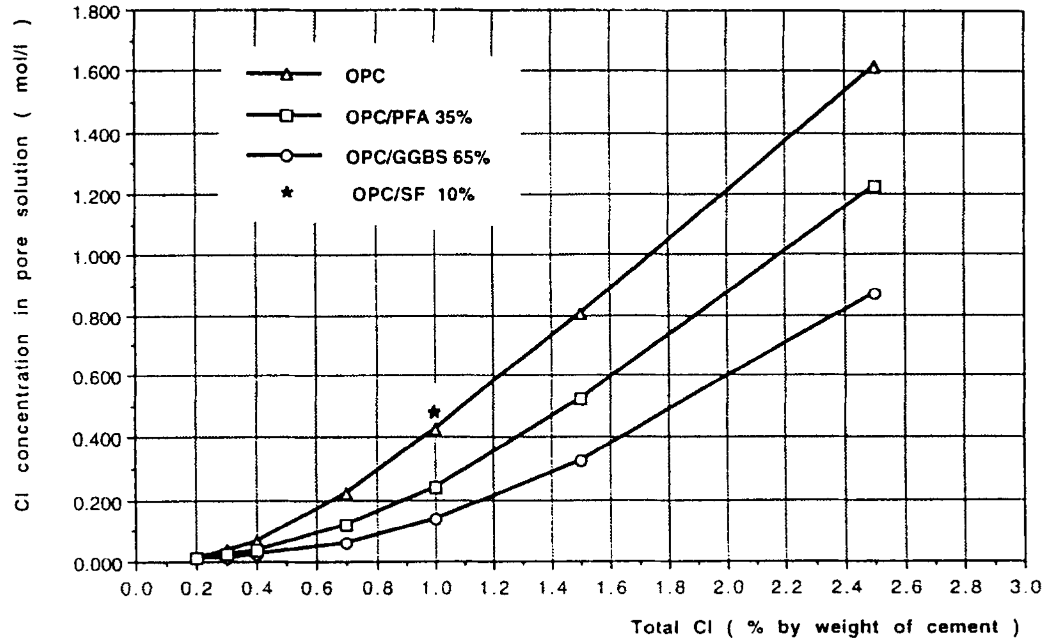


FIG. 6
Pore solution Cl^- concentration vs. total chloride content for 28 day old pastes with w/c=0.5 containing internal chloride from NaCl

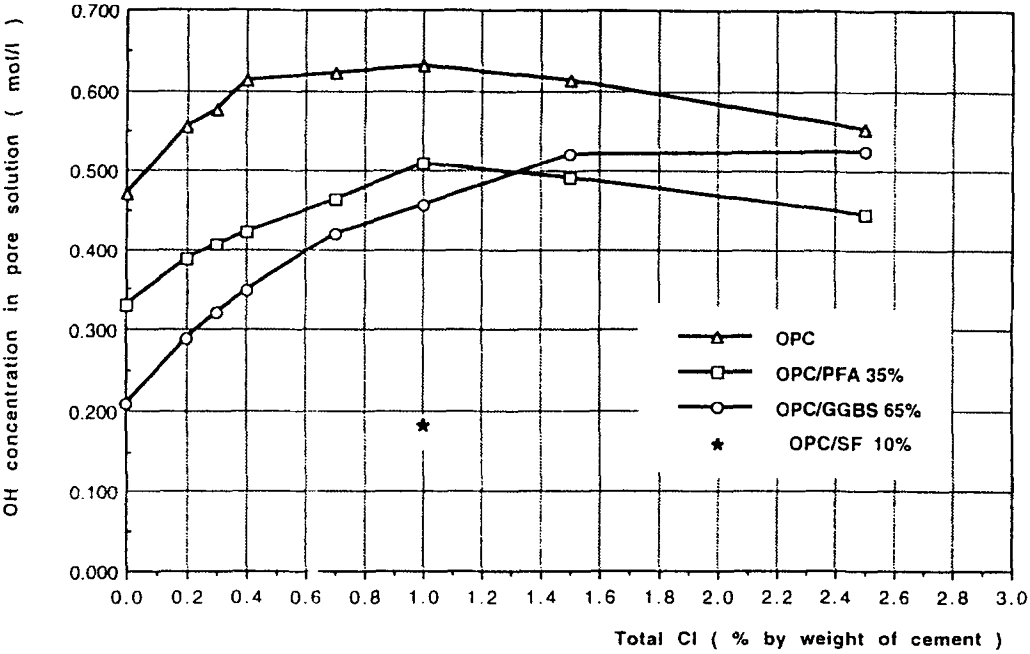


FIG. 7
Pore solution OH^- concentration vs. total chloride content for 28 day old pastes with w/c = 0.5 containing internal chloride from NaCl

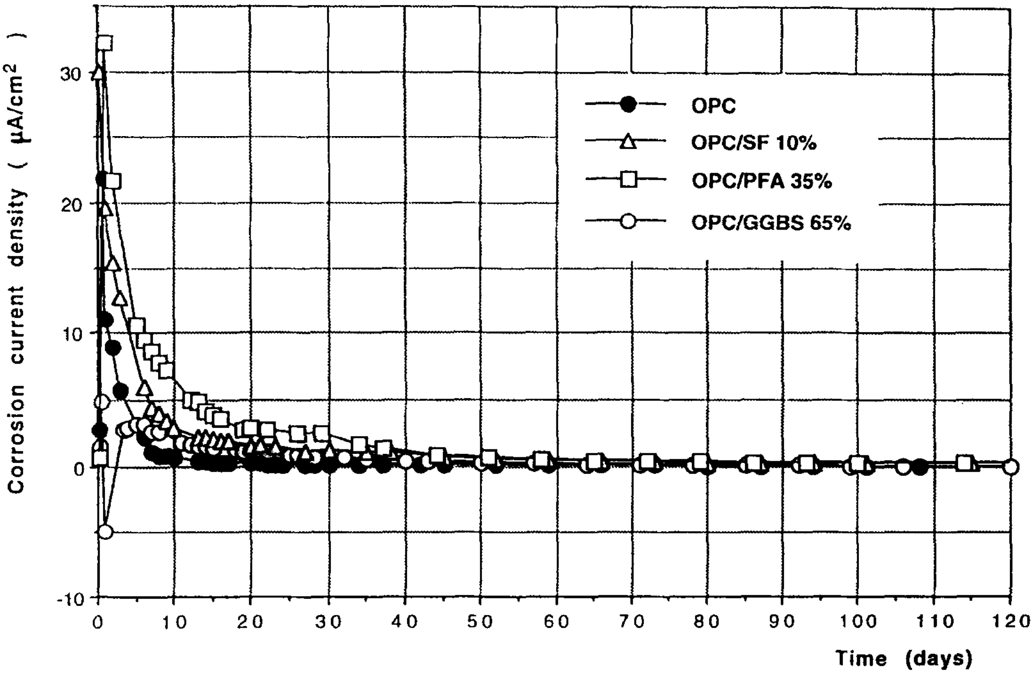


FIG. 8
Anode current density for mixes containing 1% internal chloride (by weight of cement) from NaCl

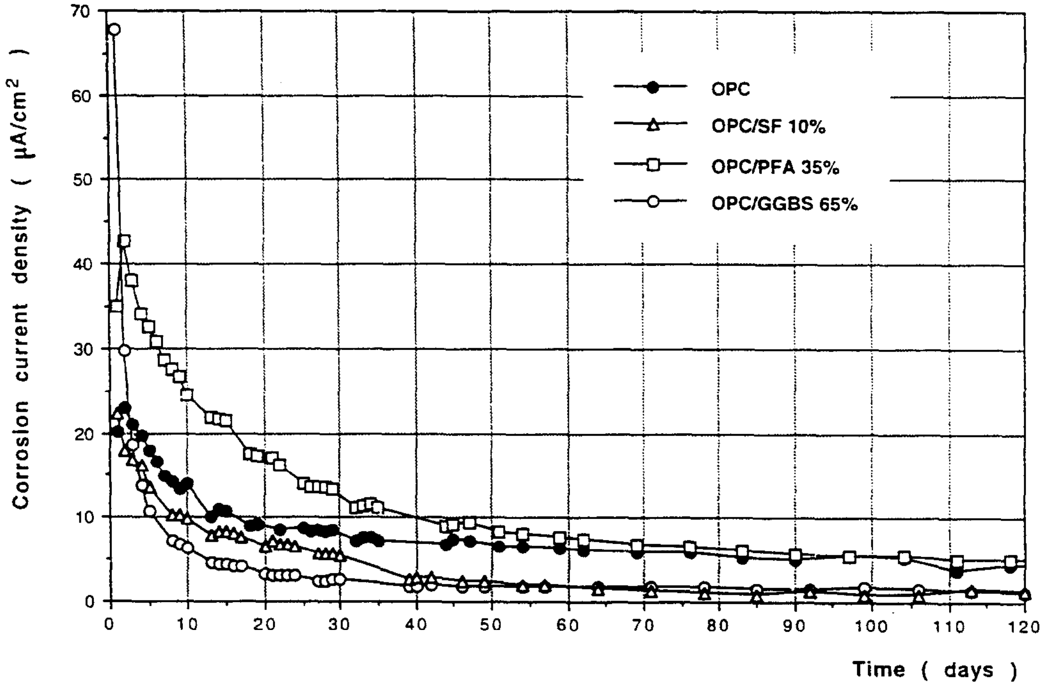


FIG. 9
Anode current density for mixes containing 3% internal chloride (by weight of cement) from NaCl

suggests that, for a given mix, the free chloride content is a significant factor determining the rate of corrosion. A high free chloride content may give a high concrete conductivity.

Mixes containing PFA (C1 and C3) experienced higher rates of corrosion, particularly at the 1% Cl^- dosage level, than those containing OPC alone (A1 and A3). This was in spite of the fact that PFA has a significantly higher Cl^- binding capacity than OPC which suggests that the OH^- concentration also influences the rate of corrosion. However, this may not be universally true when the corrosion behaviour of the silica fume concretes is considered.

As pointed out above, Mix 4 containing 90% OPC and 10% silica fume had the highest Cl^- concentration and the lowest OH^- concentration i.e. highest $[Cl^-]/[OH^-]$ ion ratio, which suggested that concretes made with silica fume should experience high rates of corrosion. However, corrosion cell D3 experienced the lowest rate of corrosion (Fig. 7). This suggests that the effect of $[Cl^-]/[OH^-]$ ion ratio on reinforcement corrosion in silica fume concretes may be secondary. Page and Havdahl [7] have reached similar conclusions in their studies on the corrosion behaviour of steel in microsilica cements [7]. Later studies by Lambert et al [8] show, however, that this finding may not be applicable to concretes made with OPC and sulphate resisting Portland cement. Permeability measurements [9] show that silica fume concretes have considerably higher permeabilities than concretes of similar mix proportions but with OPC+GGBS. However, these results are based on diffusion of chloride ions but it is the rate of transport of oxygen and ferrous ions which are important in this study and which presumably display very different characteristics.

Conclusions

The investigation into the relationship between chloride binding and reinforcement corrosion has found that generally chloride binding is not related in any simple way to rate of corrosion. For 1%

Cl^- introduced at the time of mixing, the rate of corrosion with OPC was lower than PFA and GGBS despite the fact that chloride binding occurred in the order of: GGBS > PFA > OPC. However at 3% Cl^- dosage, GGBS and silica fume performed far better than OPC. With GGBS this improvement was partly due to the fact that the differences in OH^- concentration in OPC and GGBS were less pronounced and partly due to the superior chloride binding capacity of GGBS which resulted in a lowering of the Cl^- concentration in the pore solution. The low rate of corrosion with silica fume at 3% Cl^- may be related to diffusion of oxygen and ferrous ions rather than the pore solution chemistry. Generally, PFA mixes performed rather poorly, due to their modest chloride binding capacity and reduced OH^- concentration due to pozzolanic reactions.

Acknowledgements

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