2013-02-01

Exposure of Mortars to Cyclic Chloride Ingress and Carbonation

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The presence of chloride ions is one of the primary factors causing the degradation of reinforced concrete structures. An investigation to monitor ingress of chlorides during a 24-week wetting and drying exposure regime to simulate conditions in which multiple-mode transport mechanisms are active was conducted on a variety of binders. Penetration was evaluated using free and total chloride profiles. Acid extraction of chlorides is quantitatively reliable and practical for assessing penetration. X-ray diffraction was used to determine the presence of bound chlorides and carbonation. The ability of the cement blends to resist chloride penetration was, from best to worst, ground granulated blast-furnace slag, microsilica, pulverised-fuel ash, Portland cement. The effect of carbonation on binding capability was observed and the relative quantity of chlorides also showed a correlation with the amount of chlorides bound in the form of Friedel's salt.

Introduction

Chloride ingress is the most significant cause of corrosion of reinforcing steel embedded in concrete. For corrosion to occur, the passivating film that protects steel in concrete has to be destroyed and both oxygen and sufficient humidity have to be present at the steel. Chloride ingress is one of the primary causes of passivating film destruction. When chloride ions reach the protective passive film on the surface of the reinforcing steel, they destroy the film, making the steel at that region act as an anode, while the remainder of the steel surface acts as a cathode (Neville, 1995). When the concrete surrounding the steel is wet, an electrolytic cell is completed and the steel starts to corrode. As modern concretes are free from internal chlorides, in general corrosion due to chlorides is caused by those penetrating through the concrete cover from the external environment. This movement of chlorides can be represented by an increasing chloride concentration over time, which, if monitored in relation to the position of the reinforcement, will provide an indication of the service life of a reinforced concrete structure. Furthermore, sufficient quantities of chloride ions are required to depassivate the reinforcement. This quantity is known as the threshold chloride content. Therefore, the distribution of chloride ions within reinforced concrete is of great importance. Chloride ingress is a complex process as there are different mechanisms by which chlorides can penetrate concrete depending on the local physical conditions.

Chloride transportation and quantification

The ingress of chlorides is generally caused by three mechanisms – absorption, permeation and diffusion.

- Permeation is the mechanism by which fluid passes through a material due to a hydrostatic pressure differential resulting in a saturated or partially saturated capillary flow (Kropp, 1995).
- Liquids can penetrate into cementitious material by means of absorption, as a result of surface tension acting in empty capillary pores (Kropp, 1995).
- Diffusion is defined as ionic/molecular transport from an area of high concentration to low concentration, due to random motion of molecules, until a state of equilibrium exists.

It is often the measurements of the coefficients of these transport mechanisms that are used to define the durability of concretes, although it should be noted that it is often a combination of these mechanisms that leads to chloride ion movement. It may thus be argued that a more realistic approach is to define an apparent diffusion coefficient that includes all of the transport phenomena based on obtained chloride profiles within the concrete, rather than pure diffusion. The movement of liquid, which may contain aggressive agents such as carbon dioxide or chloride ions, can be described as convection and can be caused by permeability or absorption.

The pore network enables the transportation of solids, liquids and gases through the cementitious material. As the binder type influences the microstructure of the hydrated cement paste (HCP), it will therefore have an influence on its permeation properties. In the case of permeability, a review by Kropp (1995) suggested that only pores greater than $0.1\ \mu m$ diameter can transport water under pressure. For transport to occur, these pores must also be continuous. The shape of the pores will also affect

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the transport of liquids as a pore with a large surface area can trap a large amount of water, thus slowing the transportation, as well as providing more sorption sites.

The effect of ground granulated blast-furnace slag (GGBS), pulverised-fuel ash (PFA) and silica fume (microsilica (MS)) is to reduce permeability. The reason for this reduction is mainly due to the pozzolanic reaction of calcium hydroxide (Mehta and Monteiro, 2006). It has been suggested that binders will increase the porosity of the HCP but the pores formed are discontinuous and thus permeability will be reduced (Jiang *et al.*, 1999; Ramezanianpour and Malhorta, 1995). As an alternative, it has been suggested that they favour the formation of smaller and less permeable capillaries (Kropp, 1995). Relevant to all the transport mechanisms, for transport to occur the pores must be continuous and the effectiveness of the transport through continuous pores will also be affected by the size of the pores.

Chloride binding

As stated earlier, there is a critical concentration of chloride ions required to initiate corrosion within reinforced concrete, but this concentration is complex to define due to the phenomenon of chloride binding. Owing to the structure of HCP, chlorides contained within it can exist in two forms – free chlorides and bound chlorides. Free chloride ions are dissolved in the concrete pore solution and bound chlorides are either physically bound by being adsorbed on the surface of the gel pores or chemically bound by being incorporated in the products of hydration (Kropp, 1995; Neville, 1995). The two types of chlorides normally exist together to maintain chemical equilibrium (Kropp, 1995; Neville, 1995; Nilsson, 1995).

The phenomenon of chloride binding has a benefit to steel embedded in concrete. Its effect on the corrosion of reinforcing steel is twofold (Kropp, 1995; Martin-Perez, 2000).

- Binding, which reduces the quantity of chlorides in the pore solution, reduces the amount of chlorides available for transport and therefore delays chloride ingress into concrete.
- It is generally accepted that only chlorides in the pore solution can contribute to reinforcement corrosion. Therefore, binding of chlorides allows a greater quantity of total chlorides to be present before corrosion will begin.

Thus it is only the free chlorides that can cause corrosion. It is generally accepted that the chlorides contained within the pore fluid are free chlorides and it is known that the amount of chlorides that are bound physically and chemically is affected by mineral admixtures (Arya and Xu, 1995; Lu *et al.*, 2002). The increased surface area of supplementary cementitious materials (SCMs) creates more sites for physical binding, through the increase of C-S-H, while the chemical composition (mainly an increase in aluminate contents (Table 1)) contributes to an increased capacity for chemical binding (Thomas *et al.*, 2011; Yuan *et al.*, 2009). Suryavanshi and Swamy (1996) noted that 'the solubility of Friedel's salts increases with the degree of carbonation of the concrete'. Although Nilsson (1995) noted that chloride binding increases with decreasing pH, which could be brought about from the incorporation of SCMs as well as carbonation, he also noted that the effect of carbonation on chloride binding is more significant than that of reduced pH alone.

Research significance

Deterioration of rebars due to chloride-induced corrosion is the largest single durability challenge facing reinforced concrete.

Chemical and physical composition: %	PC	PFA	GGBS	MS
SiO_2	19·88	59·01	35·20	92
Al_2O_3	6·03	22·80	13·96	0·7
Fe_2O_3	2·73	8·80	0·25	1·2
CaO	64·45	2·38	41·21	0·3
MgO	1·69	1·39	8·18	0·2
SO_3	3·14	0·27	—	0·3
K_2O	0·78	2·80	0·42	1·8
Na_2O	0·13	0·74	0·19	1·5
Cl	0·007	—	—	—
TiO_2	—	1·15	0·57	—
Mn_2O_4	—	0·08	0·55	—
MnO	—	—	0·49	—
P_2O_3	—	0·39		—
Specific surface area: m^2/kg	322	340	600	20 000

Table 1. Chemical and physical composition of binders

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This paper considers the movement of total and free chlorides, binding and the influence of carbonation on the ability of binders to chemically bind chlorides. In reality, reinforced concrete under severe conditions (such as wetting and drying) will be extremely vulnerable to deterioration. For this reason, realistic and severe conditions of wetting and drying were used in the exposure regime. Carbonation was not prevented as multiple-mode mechanisms are possible and can vastly accelerate deterioration, particularly when cement replacement materials are used.

Experimental procedure

Specimen preparation

Four mortar mixes were used in this study, incorporating Portland cement (PC), PFA, GGBS and MS. The chemical and physical compositions of the binders are shown in Table 1 and details of all the mixes are given in Table 2. It should be noted that the results presented later in the paper are valid for the composition of the materials used in this study; the results may vary for materials with different chemical compositions. A water/binder ratio of 0·42 was chosen for all the mixes so as to produce reasonable workability in the range of 350–450 mm. The aggregate/binder ratio was 1·67 for all mixes. The specimens were prepared from slabs of size $250 \times 250 \times 100$ mm. Three slabs and three cubes were cast per mix, totalling 12 for use in the experiment.

The specimens were manufactured according to BS 1881: 125 (BSI, 1986) using a pan mixer. As four different mixes were used, only one mix was cast per day. This allowed all the specimens to be manufactured in one week. The specimens were removed from the moulds 24 h after casting.

Curing, preparation and chloride exposure

After demoulding, the specimens were stored in a water bath ($20 \pm 1^{\circ}$C) for 3 days. They were then removed from the water bath and transferred to a constant-temperature room at $20 \pm 1^{\circ}$C, $55 \pm 1\%$ relative humidity for continued hydration until they were 28 days old. After 28 days, a total of 27 60 mm cores were cut from the three slabs manufactured for each mix. The cores were cut from the slabs before exposure to the chloride environments since water was used as the coolant during coring and

would have affected chloride distribution. Three 100 mm cubes were tested for compressive strength at the age of 28 days.

After conditioning at $20 \pm 1^{\circ}$C and $55 \pm 1\%$ relative humidity, the cores were coated on the circumference with two coats of epoxy emulsion (Sikaguard 680), forming a barrier that prevented any lateral ingress of chloride ions. To facilitate ponding, a 60 mm diameter pipe of 50 mm length was placed over the top of each core, forming a reservoir in which a salt solution could be contained. The joint between the pipe and the core was tight and packed with silicone sealant to ensure no leakage occurred during ponding. After the pipe was attached to the cores, they were transferred to a constant temperature and humidity room at $20 \pm 1^{\circ}$C, $55 \pm 1\%$ for exposure to the chloride environment. The cores were ponded with a 0·55 M (3·2%) sodium chloride solution for 1 day. The following day, the saline solution was removed and surface washed with deionised water to mimic the effect of rainwater and then exposed to air for 6 days. This regime was chosen to simulate real exposure conditions in a splash zone, which Bamforth (1997) identified as the most extreme zone with regard to the accumulation of surface chlorides. This wetting and drying exposure has also been used by previous researchers (Hong and Hooton, 2000; Polder and Peelen, 2002). This cycle was repeated every week for 24 weeks.

Measurement of acid-soluble chloride

The acid-soluble chloride content of the various mixes was determined after 24 weeks of ponding. Dust samples were obtained from the sample at discrete depths by slicing with a precision saw. Isopropanol was used as the coolant in the saw to prevent washout of the chloride ions. Displacement of the pore fluid by the isopropanol was unlikely as it can normally only be achieved with heavy liquids under centrifuge conditions (Cromie et al., 2002). The resultant discs were representative of discrete depths within the mortar (0–3 mm, 5–8 mm, 10–13 mm, 15–18 mm, 20–23 mm, 25–28 mm, 30–33 mm and 35–38 mm). These discs were then ground to dust using a mortar and pestle. The chlorides were then extracted from the dust samples using nitric acid by the method described in BS 1881: 124 (BSI, 1988). Using this method, all the acid-soluble chlorides are extracted and this is generally accepted as extracting the total chlorides

Mix	Binder	PC	PFA	GGBS	MS	FA[a]	Water[b]
PC	100% PC	734	—	—	—	1226	308
PFA	70% PC, 30% PFA	496	213	—	—	1184	298
GGBS	50% PC, 50% GGBS	363	—	363	—	1213	305
MS	90% PC, 10% MS	654	—	—	73	1214	305

[a] Fine aggregate (2 mm maximum size).
[b] Does not include additional water added to alter aggregate from oven dry to saturated surface dry state.

Table 2. Mix design (kilogrammes) used in experiments to yield 1 m^3 of mortar

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(Hong and Hooton, 2000; Mohammed and Hamada, 2003) although some authors have shown it to represent only 90% of the total chlorides (Glass *et al.*, 1996).

Measurement of free chloride concentration

The pore fluid chloride content was determined for each of the mortars after 24 weeks of cyclic exposure to the chloride environment. To obtain the chloride concentration of the pore fluid at different depths, 21 cores (to obtain sufficient pore fluid for analysis) were sliced into 3 mm thick discs with a precision saw, using isopropanol as described above. The resultant discs were representative of a discrete depth range within the mortar (0–3 mm, 5–8 mm, 10–13 mm and 15–18 mm). The pore fluid was expressed from these discs using a pore fluid expression device (Bjork, 2002). The chloride concentration was then determined using potentiometry with a technique similar to that described by Haque and Kayyali (1995).

X-ray diffraction (XRD) analysis of dust

The purpose of this test was to use XRD to determine the morphology of dust samples extracted from the mortar mixes. Once again, dust was extracted from discrete layers for analysis. XRD can be used to determine the presence of various compounds within powder; XRD thus allows determination of the presence of Friedel's salt and will help to determine if chlorides have become bound in this form. This test does not accurately quantify the amount of chemically bound chloride ions but will allow the various mixes to be ranked in terms of chloro-aluminate quantities. The XRD scan was also used to determine the presence or absence of peaks associated with calcium carbonate, thus indicating if carbonation had occurred. The X-ray source was copper (with a K radiation wavelength of 1·5418 Å) and the sample was scanned from 5 to 25° and 28 to 50° 2θ with a step size of 0·016° 2θ.

Results

Acid-soluble chloride distribution

The acid-soluble chloride content was plotted against depth and hence a total chloride concentration profile was developed for each mix. These total chloride profiles are shown in Figures 1–4. The free chloride concentration measured in the expressed pore fluid will be discussed later.

The profiles generally show a high chloride concentration at the surface and a decreasing concentration with depth. This is what would be expected as the external chloride source was at the surface where the concentration is high and the concentration decreases with depth as the mortars resist the penetration of the chloride ions.

The apparent diffusion coefficient was calculated for each of the mixes using a non-linear curve fitting method (Nordtest, 1995). This method provides a solution to Fick's second law of diffusion, which is commonly used to model the diffusion of chlorides into concrete. The calculated diffusion coefficients are shown in
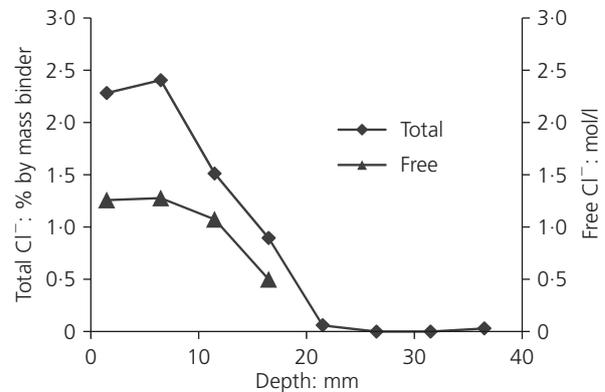

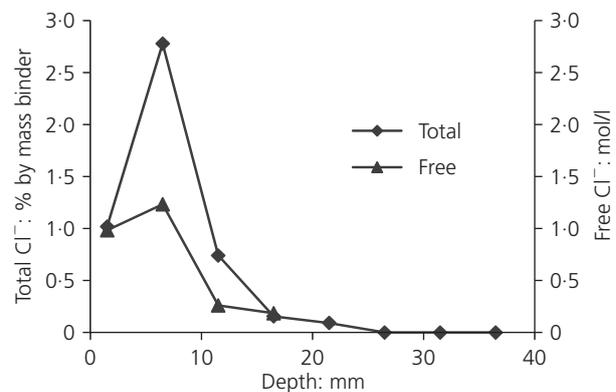**Figure 1.** Total and free chloride profile for PC mix

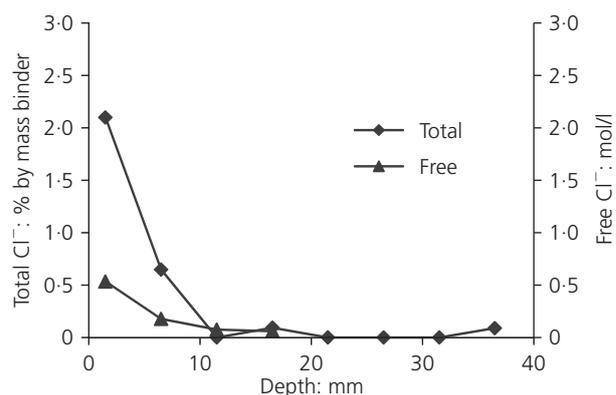**Figure 2.** Total and free chloride profile for PFA mix

Figure 3. Total and free chloride profile for GGBS mix

Figure 5 (calculated omitting the first data point due to near-surface absorption).

Free chloride concentration distribution

The free chloride concentration is considered to be the same as the chloride concentration of the pore fluid, as only chlorides that are not chemically or physically bound are free to dissolve in the pore fluid. The pore fluid chloride content was plotted against depth and
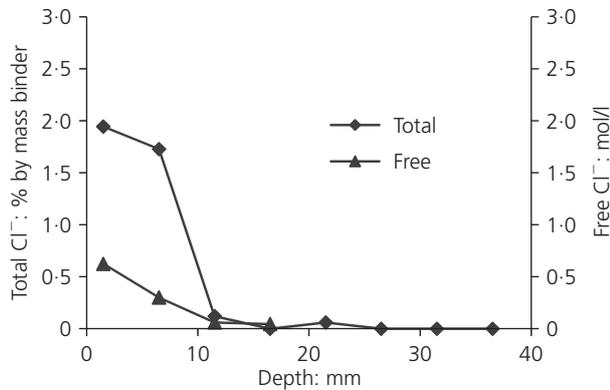
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Figure 4. Total and free chloride profile for MS mix

Figure 5. Apparent diffusion coefficient
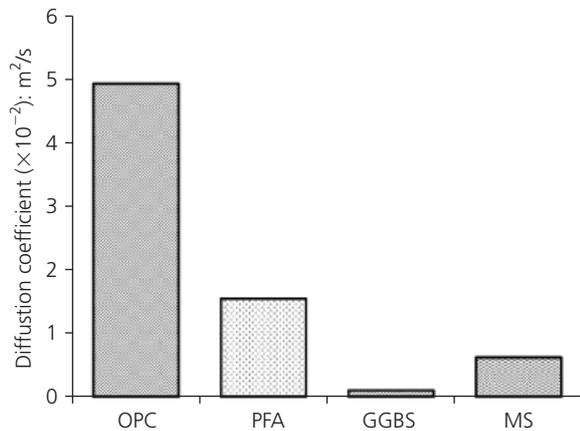

Figure 6. Quantity of calcium carbonate

Figure 7. Quantity of Friedel's salt

hence the free chloride concentration profile was developed for each mix. The free chloride profiles are also shown in Figures 1–4.

Similar to the total chloride profiles, the profiles show a high chloride concentration at the surface and a decreasing concentration with depth. This is what would be expected as the mixes were initially chloride free, the chloride source was external and, over time, chlorides began to penetrate the matrix.

X-ray diffraction analysis of dust

The XRD patterns were analysed to determine the presence of Friedel's salt and calcium carbonate. The presence of calcium carbonate was used as an indicator of the occurrence of carbonation. The relative count of calcium carbonated peaks is presented in Figure 6. The quantity of Friedel's salt for each sample, as determined from the peak count in the micrographs, is presented in Figure 7. This is termed the relative quantity between mixes.

Discussion

Acid-soluble chloride distribution

The profiles for PC (Figure 1) and PFA (Figure 2) mixes have a lower chloride concentration in the surface layer and a peak is
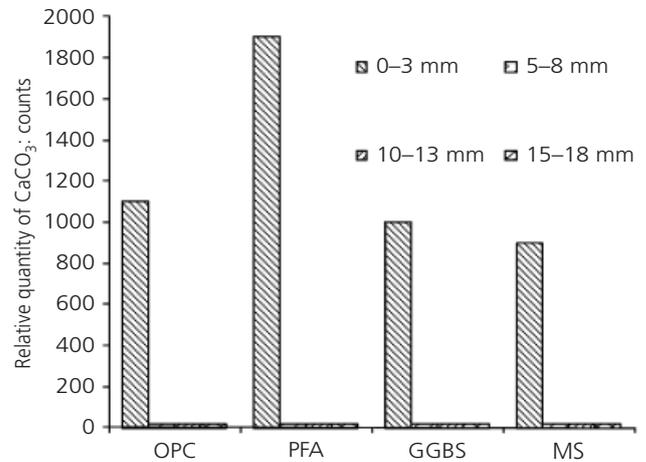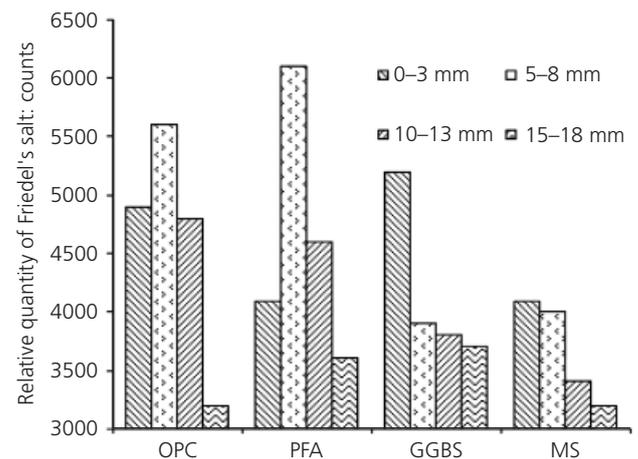
observed at a depth of just over 5 mm. The reason for the lower chloride concentration at the surface may be due to the ponding regime used with the application of deionised water removing surface chlorides. With the free chloride concentration decreasing more than the total chloride concentration (i.e. chlorides washed out rather than solubilisation of Friedel's salt), the profile would tend to indicate that this effect was achieved. However, this effect was less evident on the MS and GGBS samples due to the denser matrix and less continuous pore structures respectively that these materials produce, as reported by Lea (1998) and Maso (1996). A second reason for the peak occurring at some depth can be attributed to carbonation. It is known that carbonation, owing to the lower pH displacing previously bound chlorides, has the effect of pushing chlorides further into concrete (Ihekwaba, 1996) and thus the PFA mix, which is more susceptible to carbonation (Papadakis, 2000), had carbonated and displayed this effect.

The inclusion of GGBS, MS and PFA all had the effect of reducing the apparent diffusion coefficient relative to the PC mix

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(Figure 5). The reduction in the apparent diffusion coefficient can be attributed to both chloride binding (Bamforth, 1997) and decreased permeability (Lea, 1998).

Water-soluble chloride distribution

Although the ponding source solution was 0·55 M sodium chloride, the chloride concentration in the pore water reached 1·28 and 1·23 moles per litre (1·28 and 1·23 M) in the PC (Figure 1) and PFA (Figure 2) mixes respectively. This is caused by the build up of chlorides in pores as a result of the ponding regime used, which allowed evaporation of water after saturation, leaving chlorides behind. When the specimen was ponded again during the next cycle, the chlorides already present would have been dissolved into the new saline solution, increasing the concentration beyond 0·55 M. Thus, the concentration of chlorides can increase beyond that of the source solution with repeated cycles of wetting and drying.

The profiles were examined by comparing the peak chloride content and the chloride distribution. The highest peak chloride concentration was obtained in the PC, then PFA, MS and GGBS mixes. As the testing regime was the same for all the mixes, the difference in the peak chloride concentration was a result of the varying properties of the different binders. The two properties of particular concern in this case are the permeation properties and the chloride binding capacity of each material. The chloride binding capacity is of particular interest for the free chloride profiles as each profile will be influenced by the binding ability of the material.

Figure 1 shows that the PC mix displayed a high peak concentration of free chlorides (1·28 mol/l) and penetration to 18 mm. The profile in Figure 2 for the PFA mix shows an initially high chloride concentration followed by a moderate rise in chloride content at the second data point. This is in contrast with the total chloride content, which shows a large rise in concentration at the second data point. This can be explained as the inclusion of PFA, with its increased aluminate content (Table 1), would be expected to increase binding (Thomas *et al.*, 2011) and hence lower the free chloride concentration in the pore solution. The surface layer of PFA was carbonated (Figure 6) and, because of the lower pH, limited binding occurred; the specimen from the second data point was uncarbonated (Figure 6) and binding did occur (Figure 7). The profile for GGBS (Figure 3) shows a much lower peak concentration of chlorides and less penetration into the material than the PC mix. This can be attributed to the denser pore structure produced as a result of the hydration of the GGBS particles (Nilsson, 1995), the increased number of physical binding sites available due to the larger specific area respectively and the increased aluminate content (Table 1). The profile for the MS (Figure 4) shows a relatively low chloride concentration in the pore fluid extracted from the sample closest to the surface and a gradual decrease to lower concentrations with depth. Silica fume is likely to produce such a profile as it produces a very dense pore matrix, as described by Lea (1998) and Maage (2001).

The dense matrix formed was excellent at resisting chloride penetration, resulting in low chloride concentrations even close to the surface. The inclusion of MS increases the amount of C-S-H and thus increases the number of physical binding sites available. The large surface area of MS (as noted in Table 1) provides evidence for the opportunity for additional physical binding to occur. These beneficial phenomena are therefore more significant than the effect of the reduction in the alumina content of the blended cement, which decreases binding. Therefore, the profile reflects a matrix of low permeability and with a net decrease in chloride penetration.

X-ray diffraction analysis of dust

Figure 6 shows that calcium carbonate was present in the depth range 0–3 mm in all of the mixes and was absent at greater depths. It can therefore be stated that carbonation occurred to a maximum depth of 3 mm. As carbonation increases the solubility of Friedel's salt (Suryavanshi and Swamy, 1996) and it occurred in the first sample depth for each binder type, the comparison of Friedel's salt will be for the second sample depth.

The results revealed that the specimens with the greatest to least quantities of Friedel's salt were PFA, PC, MS and GGBS. These results were not unexpected: it is known that Friedel's salt is formed by chloride ions combining with calcium aluminate hydrate present in the mortar. PFA contains a high quantity of alumina (Al_2O_3) and therefore would be expected to increase the binding. The GGBS mix showed a decrease in binding. As the relative quantity of chlorides was less in the GGBS mix (Figure 5) there was less opportunity for Friedel's salt to form. This can be observed in Figure 7, which shows that the relative quantity of Friedel's salt that can form increases with total and free chloride concentration. The literature reports that GGBS can cause both decreases (Kropp, 1995; Mohammed and Hamada, 2003) and increases (Babu, 2001; Nilsson, 1995) in binding, depending on the composition of the material and the quantity used. Although the quantity of MS was small, as it had no alumina it would have decreased the overall amount of calcium aluminate hydrate present in a matrix as well as decreasing the permeability. Therefore, the MS would decrease the amount of chlorides that could enter and be chemically bound.

Although XRD can be used to determine if chlorides have been bound by the formation of Friedel's salt, this only accounts for the chlorides that have been chemically bound. Chlorides can also be physically bound by being adsorbed onto the pore walls within the HCP. These chlorides cannot be detected by XRD and therefore only part of the binding effect is accounted for using this test.

Comparison of free and total chloride

Figure 8 shows the two types of chlorides plotted together for all binders in a binding isotherm. The data for the first near-surface sample has been omitted as it was carbonated. The figure shows an approximately linear relationship between the two – as total
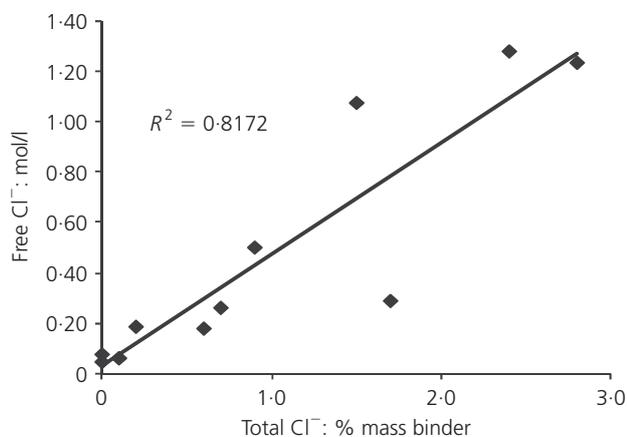
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Figure 8. Relationship between total and free chloride

chloride increases, so does the free chloride – as would be expected (Sandberg *et al.*, 1998).

The nature of the relationship is dependent on the chloride binding properties of the binders used in each mix, which is affected by carbonation. As the alumina content in each of the binders was different, it is reasonable to expect varying amounts of chemical binding in the form of chloro-aluminates to have occurred. This is reflected in the relative quantity of Friedel's salt detected in the XRD analysis of the different binders. The relationship between free and total chlorides is also affected by physical chloride binding of the chloride ions, which is influenced by the specific surface area of the binder particles. However, it is not possible to determine the degree of physical binding that has occurred. These variations have resulted in a greater spread of results. It would also be expected for there to be no relationship between individual binders for the reasons above.

Chloride profiles and XRD results

The purpose of the XRD analysis was to account for chemically bound chlorides and to help explain differences between the free and total chloride profiles. It may be argued that the presence of Friedel's salt in the matrix can partly explain the difference between the chloride concentration profiles for the free and total chlorides. As chlorides contained in the Friedel's salt will not be present in the pore water, the chloride concentration will differ from the acid-soluble chloride content, which contains most of the chlorides present in the matrix. As the units for free and total chlorides are different, a qualitative comparison was made.

The total chloride profile in the PC mix shown in Figure 1 indicates a peak in total chloride concentration at a depth of 5–8 mm, which is slightly less evident in the corresponding free chloride profile. This may be explained using the XRD results, which showed the greatest quantity of Friedel's salt at a depth of 5–8 mm: more chlorides were thus bound and the increase in free chlorides was less. The lower relative quantity of Friedel's salt in the 0–3 mm layer compared with the 5–8 mm layer can be

attributed to carbonation (Figure 6), which is known to release bound chlorides (Kropp, 1995; Nilsson, 1995).

Although the free and total chloride profiles for the PFA mortar showed the same trend, there was a relative quantity difference. The 5–8 mm layer showed a dramatic increase in total chlorides (>150%) compared to the surface layer, but the free chloride profile revealed a less significant change. This is explained by the XRD results, which showed significantly more binding in the form of Friedel's salt in the 5–8 mm layer. The smaller quantity of Friedel's salt, and hence binding at the surface, is likely due to the carbonation observed. This is further supported by the work of Papadakis (2000) and Sanjuan (2003) who found that inclusion of PFA increased carbonation and thus there was little opportunity for the PFA to bind surface chlorides due to carbonation.

Both total and free chloride concentrations decreased with depth in the GGBS mortar. Compared with the PC and PFA mixes, the quantity of total chlorides present is smaller, thus suggesting a lower rate of ingress. This is not unexpected: Lea (1998) reported that GGBS produced a discontinuous pore structure, while Maso (1996) reported that its inclusion resulted in less CH and less well oriented CH in the interfacial transition zone. Some Friedel's salt formed near the surface, which can explain why there was a smaller change in the free chloride concentration compared with the total chloride concentration. As the quantity of chlorides penetrating to greater depth was small, there was little opportunity for binding to occur and hence there was little Friedel's salt formed at greater depth.

The MS specimens showed low levels of chloride ingress. As silica fume is known to produce a very dense impermeable matrix (Lea, 1998) its use resulted in less chloride ions penetrating the sample and hence less Friedel's salt was evident when compared with the other mixes. The 5–8 mm layer showed a greater decrease in free chlorides compared with the total chloride profile. This is likely to be the result of some chloride binding. Silica fume does not enhance chemical binding (Arya and Xu, 1995; Nilsson, 1995) as it contains virtually no aluminates. Therefore, any chemical binding that occurs must be the result of the aluminate in the PC component of the binder. The carbonation detected in the surface zone of the silica fume has likely reduced the effect of binding in this region. Although XRD may be used to discuss the binding of chlorides, it should be remembered that it can only be used to identify chemically bound chlorides and does not account for physical binding.

Effect of different cement blends on chloride ingress

All the test profiles indicated that the GGBS matrix was the best at resisting chloride ingress. The overall performance of the binders – from best to worst – was GGBS, MS, PFA and PC for the materials tested in this work. All the test results indicate that the inclusion of cement replacement materials increases the chloride penetration resistance of cements.

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Conclusions

The different characteristics measured in this work, namely total chloride concentration, free chloride concentration and characterisation by XRD, all ranked the performance of the binders in the same order. The best chloride penetration resistance was provided by GGBS, followed, in order, by MS, PFA and then PC.

The effect of carbonation on binding was significant and it is recommended that it should be measured in conjunction with chloride concentration when using materials with chloride binding capability.

The total chloride profiles obtained showed a similar trend to the free chloride profiles. Although quantification of the free chlorides may be a more accurate way of assessing corrosion potential than total chlorides, it is a higher risk method as additional bound chlorides are also present and these are not accounted for. Should conditions arise that cause liberation of these additional bound chlorides (carbonation, for example), there is the potential for a massive sudden increase in free chloride concentration within the material. Total chloride content can be determined on site with the use of portable analysis methods and is therefore a versatile method of assessment of chloride ingress.

Acknowledgements

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