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Chemical profiles of cement pastes exposed to a chloride solution spray

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Abstract

This paper reports on the findings of a study of the chemistry of chloride penetration into cement pastes. Three binder combinations were used with three types of curing. At certain exposure times, specimens were sliced at 5-mm intervals, ground, and analysed using X-ray fluorescence (XRF) and thermogravimetry (TG) techniques. Up to 6-month exposure results are reported in this paper. As a result of leaching of calcium, silicon content was used to determine binder content for the XRF measurements. It was found that the vast majority of chloride permeation had occurred by absorption, and that curing by sealing in film or the addition of self-cure admixture more than halved the depth to which chlorides penetrated. In some instances, sodium was present in proportionally higher quantities than chloride, which has been attributed to the replacement of sodium ions by potassium ions.

Keywords: Curing; Hydration products; Microstructure; Diffusion; Durability

During the work carried out by the authors into the performance of self-cure concrete [1], a study of the penetration of chlorides into this material was undertaken using an exposure regime involving alternate cycles of spraying with a sodium chloride solution and drying. To complement this work, paste samples were also exposed to the same spraying regime to allow an examination of the chemistry of chloride penetration and binding. This paper reports on the findings of the paste study that has recently been completed.

1. Experimental details

Cement pastes were prepared with water/cement ratios of 0.5 and three types of binder combination: portland cement alone (PC) and portland cement combined with pulverised fuel-ash (PFA) or ground granulated blast furnace slag (GGBS) as 70% PC/30% PFA and 60% PC/40% GGBS. One mix of each binder type had 0.1 M of self-cure admixture (polyethylene glycol with an average molecular weight of 200) added during mixing (with respect to the mix water). 70-mm cubes were cast from these mixes. In this study the effects of different curing actions were investigated only after an age of 24 hours. Therefore, for the first 24 hours all specimens were kept under damp hessian. Since the aim was to examine the interactions of the chloride solution with a “real” cement paste surface, no attempt to prevent surface carbonation was made. Furthermore, subsequent to casting, no attempt was made to prevent bleeding and segregation, other than by finishing the exposed surfaces with the face of a trowel once bleed water had appeared.

The cubes were then demoulded and transferred to a 20°C/60% RH environment where the self-cure and one set of control mixes were left exposed with the as-cast faces upward and their undersides in contact with a nonabsorbent surface. Another set of control cubes was tightly sealed in waterproof film to prevent evaporation and left arranged in an identical manner in the same environment.

At an age of 28 days, five sides of the cubes were treated with a silane formulation and then coated in water-resistant wax, leaving only the as-cast face exposed. The cubes were then transferred to a chloride spray tank containing a 5-M solution of NaCl. The chloride exposure regime consisted of 12 hours spraying followed by 12 hours drying. During the drying period the environmental conditions were 20°C/60% RH, although it is likely that the persistence of water droplets in the atmosphere around the cubes meant that relative humidity was higher than this for a short period after spraying. Cubes of each binder type from each curing regime were removed at ages of 1, 3, and 6 months and left to dry in

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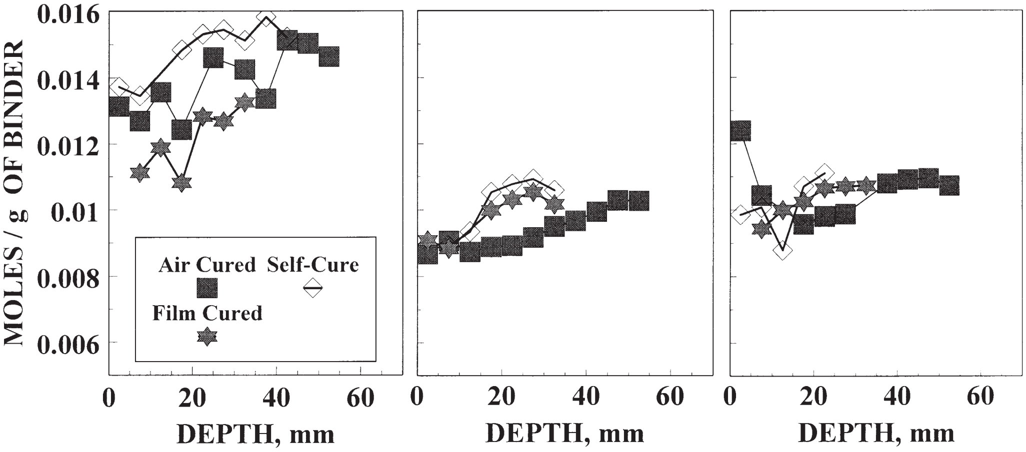

Fig. 1. Calcium profiles of different binder pastes.

air for 48 hours. 50-mm cores were taken from the centre of each exposed face. These cores were then left to dry for a further 48 hours and sliced at 5-mm intervals along their length using a diamond circular saw. The saw had a blade thickness of 1-mm, making the average thickness of each slice 4-mm. Water was used as a coolant during sawing and, inevitably, some removal of soluble material will have occurred. However, analysis of an approximately 5-mm deep

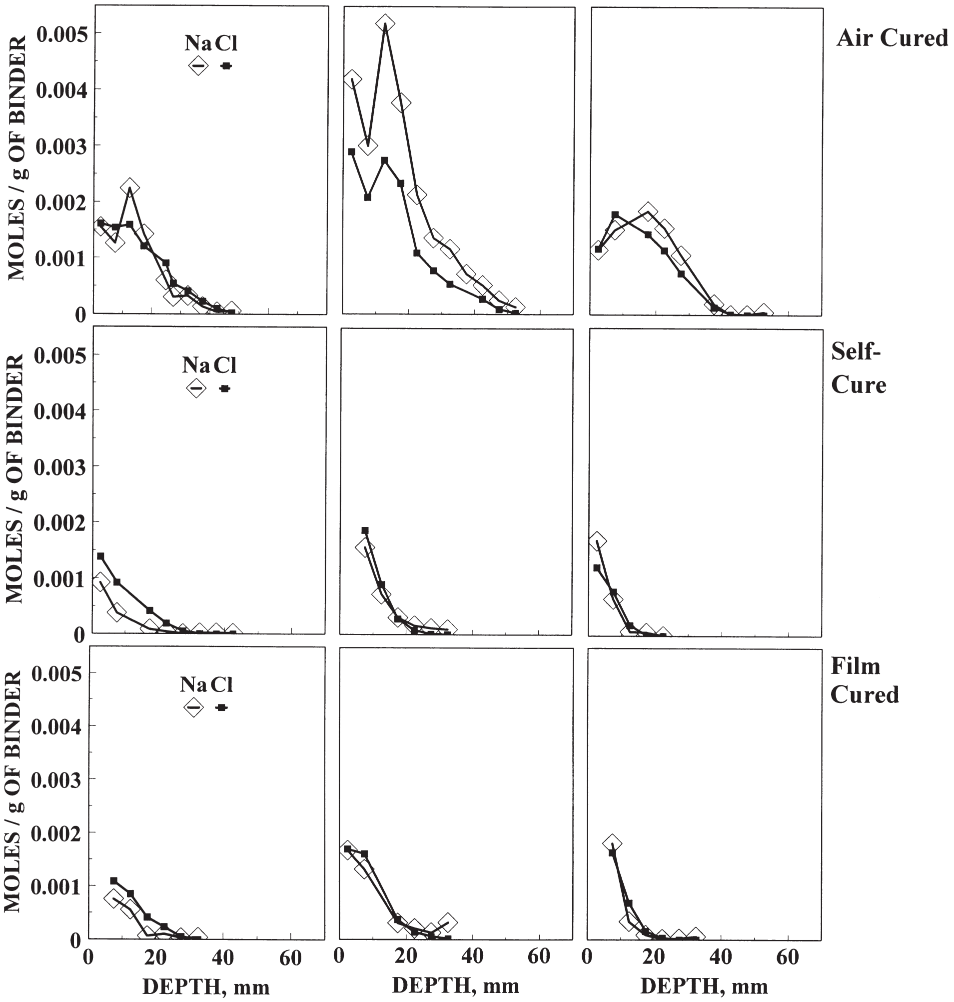

Fig. 2. Chloride and sodium profiles of different binder pastes.

fragment of the surface of an air-cured PC paste cube exposed to the same regime at the same time, removed by chiselling, indicated a difference of less than 0.01 wt% of chloride compared to the sawed slice on repeated analysis. After drying in air for 24 hour, these slices were ground in a ball mill and analysed using X-ray fluorescence (XRF) and thermagravimetry (TG) techniques. The power samples for XRF analysis were compressed into pellets.

2. Results and discussion

The results presented in this paper are almost exclusively those from 6-month-old paste specimens, for the simple reason that between ages of 1 and 6 months no detectable change in the chemical profiles was observed, indicating that the majority of movement of chemical species in that time had been the result of absorption in the first month of exposure. The exception to this is the film-cured PC paste, where the results are those for 3-months exposure due to a crack found to be present in the 6-month specimen.

The XRF results in this study are expressed as a percentage of the binder content. This was calculated using the measured silicon content (also measured using XRF), since it became clear that leaching of silicon had been much less than that of calcium during exposure. Calcium leaching can be seen in Fig. 1. It would appear that less calcium has been lost from the self-cure pastes than the others, with the air-cured paste displaying the greater amount of leaching.

2.1. Chloride and sodium content

Chloride and sodium profiles determined using XRF are shown in Fig. 2. The chloride profiles from the film-cured and self-cure specimens are very similar, which suggests that, while self-cure cement pastes still lose water when they are exposed to the atmosphere, the quality of the resulting surface is very close to that obtained when water loss does not occur at all. The air-cured specimens, however, display a much deeper penetration of both chloride and sodium ions. In fact, the depth to which chloride ions have penetrated is more than twice that observed with better curing.

A feature of the air-cured pastes is a peak in either chloride, sodium, or both elements just below the surface. It is possible that this is a result of the production of cracks as a result of drying shrinkage. Evidence for microcracking can be seen in Fig. 3, which shows a scanning electron micrograph of a fracture surface of the 15–20-mm air-cured PC paste slice. The 15-mm slice edge is located to the left-hand side of the picture, while the 20-mm edge is located to the right. Thus, the crack is running across the slice. While the performance of the self-cure paste in this instance is good, it should be noted that half-cell corrosion potential tests conducted on self-cure concrete exposed to an identical chloride spray regime displayed corrosion potentials somewhere between air-cured and film-cured controls [2].

One important feature of the chloride and sodium profiles is that, in the case of the air-cured PFA paste, more sodium ions have penetrated into the samples than chloride ions. This is clear because the ratio of sodium to chloride in molar terms is greater than one. One possible explanation of this can be illustrated by looking at these pastes' potassium profiles, shown in Fig. 4. These show that a redistribution of K^+ ions has occurred in the PC/PFA pastes. This is presumably partly a result of the highly soluble ions being leached from the paste by the chloride solution. However, the peak present in all three profiles suggests that there is also a movement of potassium ions further into the speci-

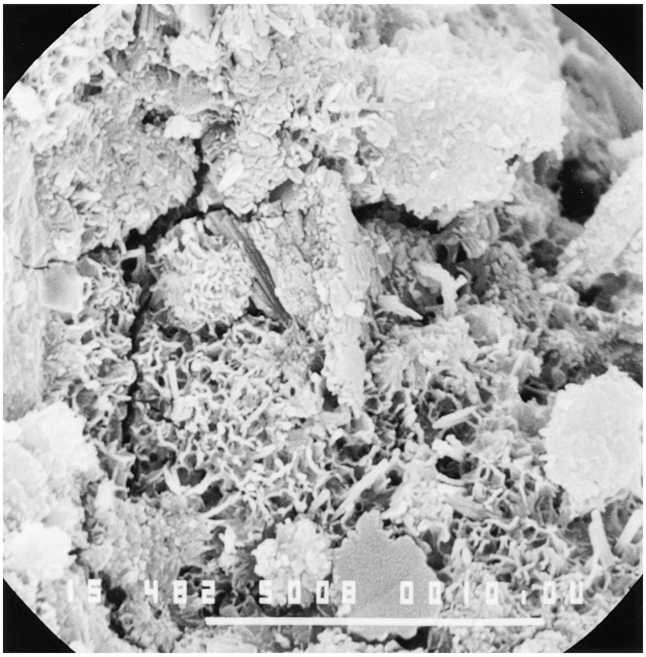

Fig. 3. Hydrated cement paste microstructure in the 15–20-mm depth slice.

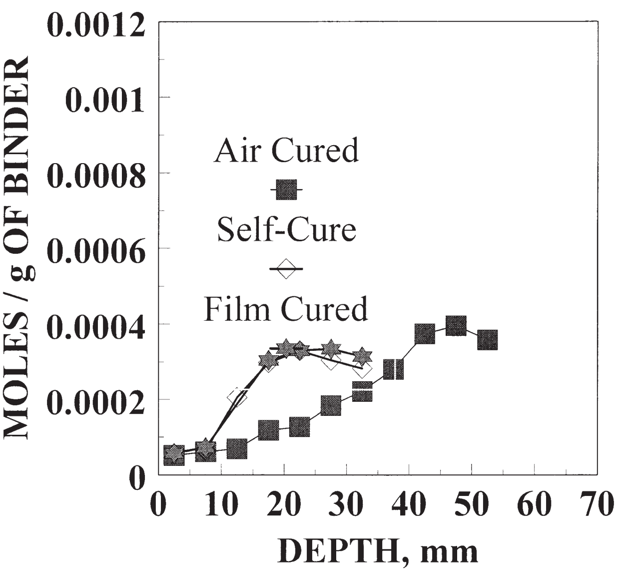

Fig. 4. Potassium profiles for PFA pastes.

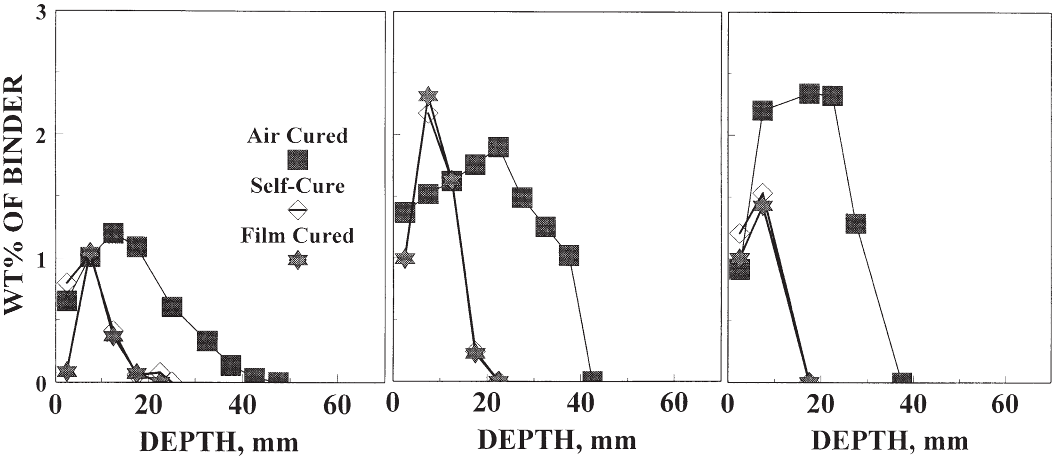

Fig. 5. Measurement of Friedel's salt dehydration at 320°C using TG.

men. Work by Xu and Hooton has shown that two of the driving forces behind the migration of alkali ions are the presence of moisture gradients (with the ions moving from wet regions to dry regions) and electric potential differences [3]. The peak in potassium content occurs in all three specimens at the depth at which chloride penetration is first detected. This is presumably the depth to which water has also penetrated and, hence, relatively dry cement paste exists beyond this point. Therefore, the former driving force is certainly one contributing factor. However, it is also likely that the ions have migrated partly as a means of balancing charge within the pore solution [4]. It is clear that the most radical redistribution of potassium ions has occurred in the air-cured specimen, in which the sodium ion content is exceptionally high. This implies that the movement of sodium into the paste in this instance is partly as a means of offsetting the charge imbalance caused by the migration of potassium. This type of potassium migration is observed in all the pastes, although it is more prominent in the PC/PFA samples due to the higher potassium levels present.

2.2. Friedel's salt and calcium hydroxide

By conducting TG on the paste specimens, it was possible to build up profiles for the distribution of Friedel's salt and calcium hydroxide (Figs. 5 and 6, respectively). This was done by measuring the weight losses observed at around 320 and 460°C corresponding to the dehydration of Friedel's salt and calcium hydroxide, respectively. It is clear that at the surface of virtually all the specimens there is a lower quantity of Friedel's salt than at greater depths below the surface. The stability of Friedel's salt is dependent on pH [5], and hence the lower quantities present at the surface can be attributed to lower calcium hydroxide levels in this region as a result of both leaching and carbonation. Beyond the surface, the Friedel's salt profiles follow the trends

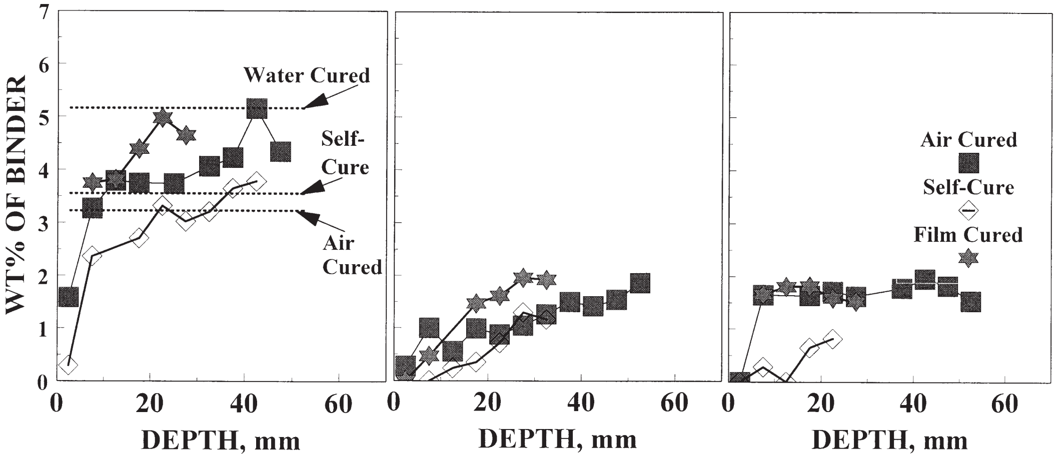

Fig. 6. Calcium hydroxide profiles (28-day calcium hydroxide levels in pastes from a previous study are indicated with dotted lines).

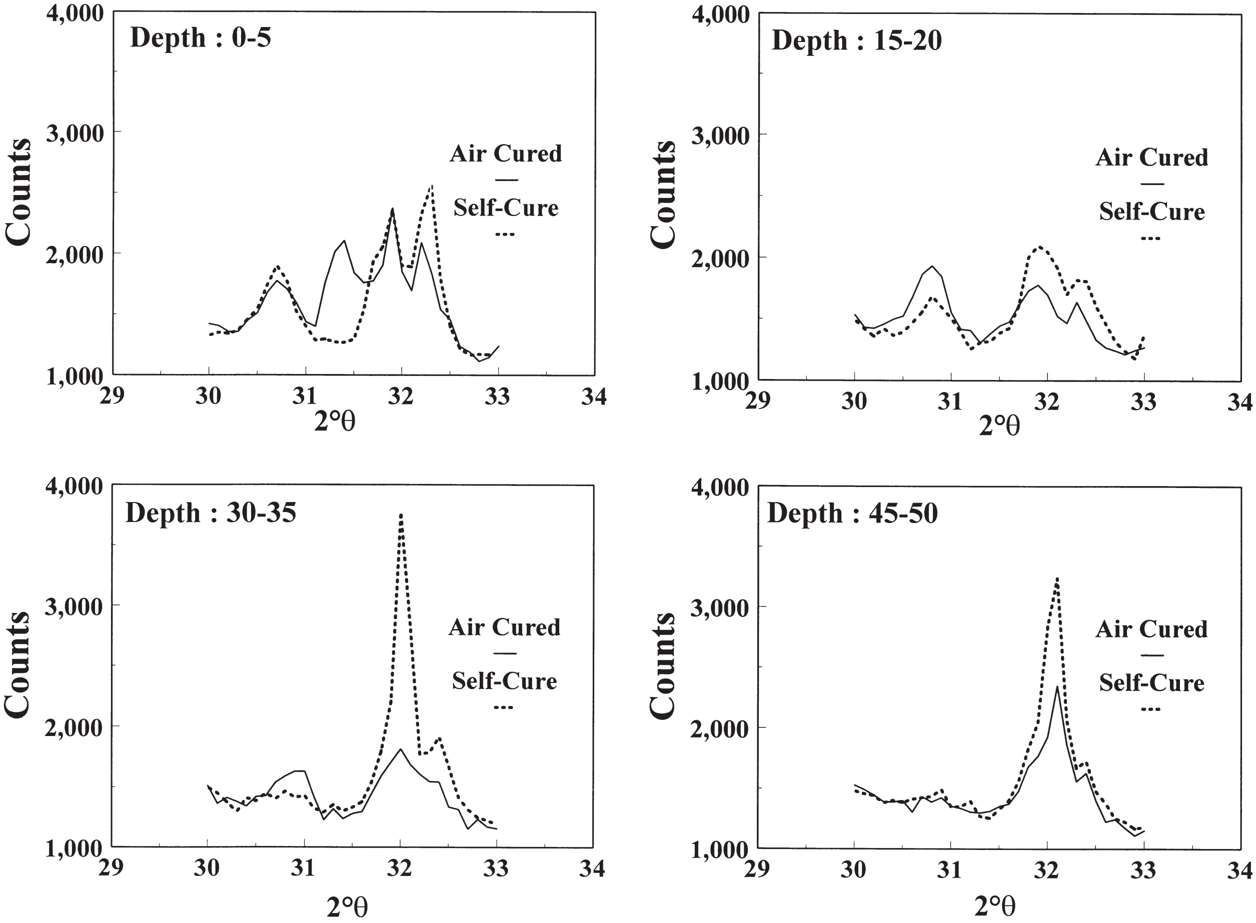

Fig. 7. XRD traces of samples taken from selected depths into self-cure and air-cured PC pastes.

shown by the total chloride measurements reasonably well. Both the PC/PFA and PC/GGBS pastes generally display higher levels of Friedel's salt than the PC, a result of the material's higher aluminate content.

An interesting feature of the profiles is that the self-cure pastes contain less calcium hydroxide than both the film- and air-cured samples. Other work has shown that the degree of hydration observed in self-cure cement pastes lies between the air-cured and film-cured controls [1], and the levels measured previously for PC pastes at 28 days are indicated on Fig. 6.

The high calcium hydroxide content of the air-cured samples must therefore be attributed to the penetrating water leading to renewed hydration of the air-cured cement. This is not the case for the self-cure pastes, which do not permit the penetration of water far below their surfaces. Furthermore, renewed hydration of the calcium silicate cement phases in the region inhabited by water in the self-cure pastes does not seem to occur, suggesting that the unreacted phases are not easily accessible to water. Fig. 7 shows the results of XRD conducted on self-cure and air-cured PC paste samples taken from various depths showing the two peaks observed between 31 and 33 °2θ which are contributed to by both C_3S and C_2S. It can be seen that at all four selected depths the quantities of the two unhydrated phases is higher in the self-cure paste—the opposite of the situation observed after 28 days of air curing [1]. The additional peaks visible in these plots are Friedel's salt at around 30.7°2θ and sodium chloride at around 31.4°2θ.

The lower calcium hydroxide levels in the self-cure specimens may explain the lack of correlation between chloride penetration and half-cell corrosion potential results discussed in the previous section. The possibility of corrosion increases as the Cl^-/OH^- ratio increases [6] and it is likely that this ratio is higher in the pore solutions of the self-cure concrete corrosion specimens than in the film-cured controls.

3. Conclusions

1. In terms of chloride ingress, the addition of the self-cure admixture followed by air curing has the same effect as film curing: halving the depth of chloride penetration compared to air-cured specimens.
2. It would appear that potassium ions moving out of and further into the cement paste are replaced by the

ingress of sodium ions when the paste is in contact with a sodium chloride solution.

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