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ASPECTS OF THE PORE SOLUTION CHEMISTRY OF HYDRATED CEMENT PASTES CONTAINING METAKAOLIN

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ABSTRACT

The hydroxide ion concentrations of expressed pore solutions of Ordinary Portland cement pastes containing 0, 10 and 20% of metakaolin by weight of cement were determined at various stages of hydration. Effects produced by two types of metakaolin, differing in degree of purity, were compared and, in each case, incorporation of metakaolin into the pastes was found to cause a long-term reduction in pore solution hydroxide ion concentration. The presence of metakaolin was also found to result in an increase in the extent to which chloride ions, introduced via the mix water, were excluded from the pore solution phase. The significance of these results in relation to the ability of hydrated cement matrices containing metakaolin to provide corrosion protection to embedded steel is considered.

Introduction

Metakaolin ($Al_2Si_2O_7$) is a largely amorphous dehydration product of kaolinite. Its pozzolanic character and potential for use in concrete and cement-based composites have been reported in several papers (1-4). Various aspects of its influence on the durability of these materials are likely to depend on the extent to which it may modify the compositions of their pore solution phase.

The work to be described in this paper was intended to elucidate compositional features of the pore solution phase in hydrated cement pastes made of Portland cement blended with various percentages of metakaolin. The effect of introducing chloride ions as a mix contaminant was also examined because of the significance of this with regard to corrosion behaviour of embedded steel.

Experimental

The chemical compositions of the materials used are presented in Table 1. Blended cements were prepared from OPC and two grades of metakaolin, labelled for the purpose of this investigation as MK501 and MK505, of differing composition with respect to minor contaminants. In order to produce powders of a consistent fineness all materials were sieved to

TABLE 1

Chemical Analysis of OPC, MK501 and MK505 (weight %)

Constituent	OPC	MK501	MK505
CaO	65.3	0.4	0.07
SiO_2	20.6	54.2	52.1
Al_2O_3	5.3	40.8	41.0
Fe_2O_3	2.6	0.6	4.3
SO_3	3.0	0.3	
MgO	1.2	0.2	0.2
K_2O	0.8	2.1	0.6
Na_2O	0.1	0.1	0.3
Cl	0.02	-	-
P_2O_5	-	0.1	
TiO_2	-	0.04	0.8
Mn_2O_3	-	0.04	
L.O.I.	0.8	1.0	0.6

150 μm. All cement paste samples were prepared in duplicate with distilled water at a water/solids ratio of 0.5 (according to the mix proportions shown in Tables 2 and 3). Blended cement pastes were produced by partial replacement of the OPC with metakaolin. Samples containing chloride ions were prepared by dissolution of the required quantities of sodium chloride in the water prior to mixing. The specimens were cast into plastic cylinders (80 mm × 49 mm diameter), vibrated to remove air, sealed, rotated about their longitudinal axes for 24 hours to minimise segregation and stored at 22 ± 2°C for periods of 1, 7, 36 and 100 days.

By means of the device described in previous investigations (5), pore solutions were expressed from duplicate paste specimens for each level of metakaolin replacement and maturity. The determination of hydroxide and chloride ion concentrations was carried out in triplicate for each pore solution. Hydroxide concentrations were obtained by titration with nitric acid in the presence of phenolphthalein and chloride concentrations were measured by a spectrophotometric method (6). The data presented in Figures 1-6 represent average values calculated from these results.

Results and Discussion

Chloride-free Specimens. The changes in pore solution pH values as functions of curing time are depicted in Figures 1 and 2. Plots C' and C" have been calculated as 90 and 80% (respectively) of the total pore solution alkali concentration of the unblended OPC paste. They are intended to represent the effects of 10 and 20% additions of an inert diluent (which neither removes nor contributes alkalis to the pore solution).

TABLE 2

Mix Proportions of Cement Paste Samples for Pore Solution Analysis (Blended with MK501)

%MK 501	% CHLORIDE	W:S RATIO	AGE (DAYS)
0	0, 0.1, 0.4, 1.0	0.5	1, 7, 36, 101
10	0, 0.1, 0.4, 1.0	0.5	1, 7, 36, 101
20	0, 0.1, 0.4, 1.0	0.5	1, 7, 36, 101

TABLE 3

Mix Proportions of Cement Paste Samples for Pore Solution Analysis (Blended with MK505)

%MK 505	% CHLORIDE	W:S RATIO	AGE (DAYS)
0	0, 1.0	0.5	1, 7, 36, 100
10	0, 1.0	0.5	1, 7, 36, 100
20	0, 1.0	0.5	1, 7, 36, 100

Comparison of the data in Figures 1 and 2 indicates that the effects of the 501 and 505 grades of metakaolin were generally very similar. Both caused a slight initial increase in the pore solution alkalinity (at 24 hours), but thereafter resulted in a lowering of the pH value to an extent which was greater than that expected for an inert diluent. Nevertheless, the long-term pH values recorded, in the range 13.4 to 13.5 for the 10% metakaolin specimens and 13.1 to 13.2 for the 20% metakaolin specimens, were well in excess of the minimum pH required to cause passivation of steel in reasonably well-oxygenated concrete (7) and were therefore not considered to be of direct concern from the point of view of the corrosion behaviour of reinforcing bars. The magnitude and time dependence of the reductions in pore solution alkali concentration of the metakaolin-containing pastes were intermediate between those recorded in previous researches into the pore solution composition of other pozzolanic cement systems containing silica-fume (5) and PFA (8). It seems likely that the effects are due to the enhanced capacity of the C-S-H gel formed by pozzolanic binders, which is of relatively lower Ca:Si ratio than that typically found in hydrated Portland cements, to remove alkali metal cations by sorption from the pore solution (9, 10, 11). This would appear to be related to the beneficial influence of metakaolin in controlling problems of alkali-aggregate reaction, as reported by other researchers (12).

Chloride-contaminated Specimens. The effects of replacement additions of metakaolin on the pore solution chloride ion concentrations for samples containing various percentages of internal chloride ions are shown in Figures 3–6. The values of the $[Cl^-]/[OH^-]$ ratio for the

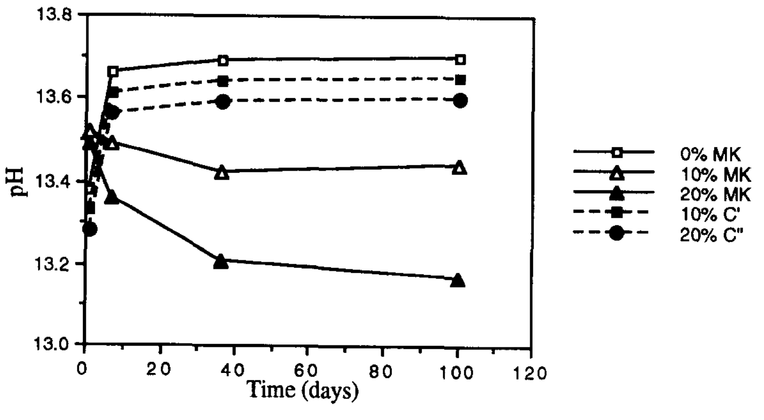

FIG. 1.
Effect of additions of MK501 on pore solution pH.

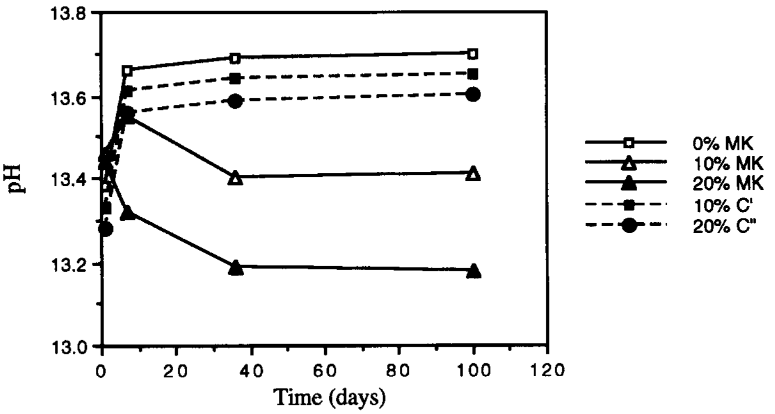

FIG. 2.
Effect of additions of MK505 on pore solution pH.

expressed pore solutions of all paste samples containing internal chloride ions are presented in Table 4.

It is clear from Figures 3 and 4 that both grades of metakaolin studied caused a substantial reduction in the concentrations of free chloride ions that were retained in the pore solution phase of paste specimens in which 1% chloride (by weight of total solids) had been included as a mix contaminant. This effect was also observed for specimens made from the 501 grade of metakaolin with 0.4% chloride, as shown in Figure 5. In specimens with only 0.1% chloride as a mix contaminant, the capacity of the cement hydration products to bind chloride ions was such that the concentrations of chloride remaining in the pore solution at ages of 36 days or longer had fallen to around 10 mmol dm^{-3}, irrespective of whether the material contained 0, 10 or 20% metakaolin, as shown in Figure 6.

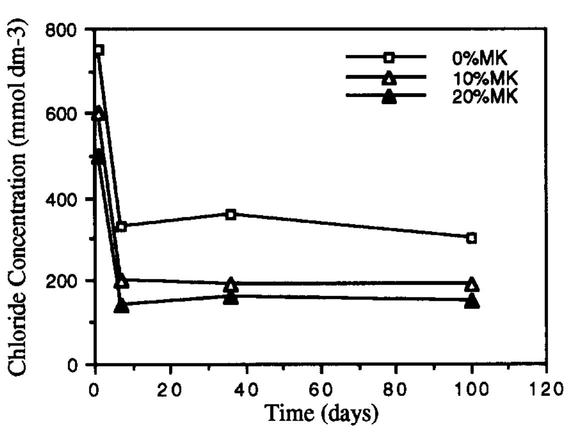

FIG. 3.
Effect of additions of MK501 on pore solution chloride ion concentration for samples containing 1.0% internal chloride ions (by weight of total solids).

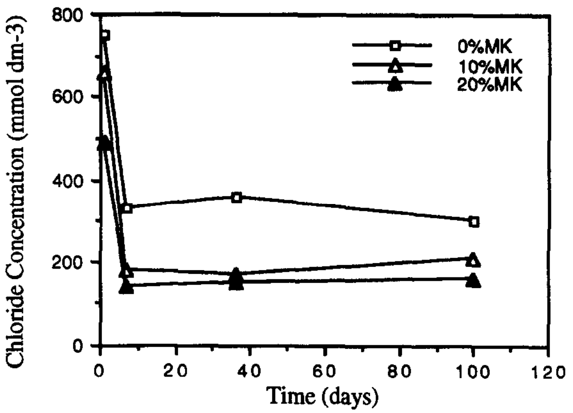

FIG. 4.

Effect of additions of MK505 on pore solution chloride ion concentration for samples containing 1.0% internal chloride ions (by weight of total solids).

Previous researches into the effects of different pozzolanic materials on the chloride-binding capacity of Portland cements have shown substantial variations in behaviour, ranging from increases in chloride-binding observed for PFA's (13, 14, 15) and certain silica fumes (13) to substantial reductions for other silica fumes (5, 16). The nature of the enhanced chloride-binding exhibited by the metakaolin-blended cement pastes used in the present investigations therefore warrants further discussion in the relation to the specific changes in solid phase hydration products that are associated with metakaolin and this will be considered in another paper (17). From a practical viewpoint, however, the significance of the findings as an indication of corrosion behaviour of embedded steel may best be understood in terms of the data recorded in Table 4.

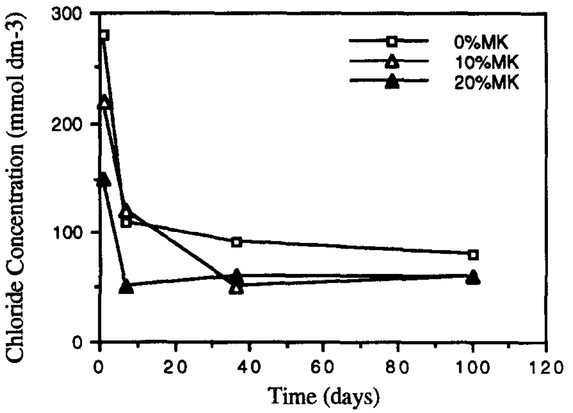

FIG. 5.

Effect of additions of MK501 on pore solution chloride ion concentration for samples containing 0.4% internal chloride ions (by weight of total solids).

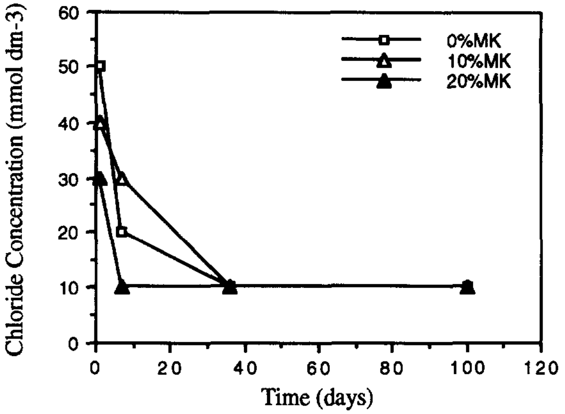

FIG. 6.
Effect of additions of MK501 on pore solution chloride ion concentration for samples containing 0.1% internal chloride ions (by weight of total solids).

For reasons which have been discussed in detail elsewhere (18,19), the ratio of the concentrations of chloride to hydroxide ions in the pore solutions, $[Cl^-]/[OH^-]$, provides a simple index for comparing the relative risks of chloride-induced depassivation leading to pitting corrosion of steel in different types of concrete. It should be emphasised, that this index is only one amongst several factors that influence the risk of chloride-induced corrosion and thus the concept of a threshold $[Cl^-]/[OH^-]$ is of limited applicability (20). Nevertheless, the values of $[Cl^-]/[OH^-]$, shown in Table 4 for the various pastes at different stages of hydration, indicate only marginal differences between the expected risks of corrosion

TABLE 4

$[Cl^-]/[OH^-]$ Ratios of Pore Solutions Expressed from Chloride-Containing Paste Samples at Various Ages

% MK	%Cl^-	1 DAY $[Cl^-]/[OH^-]$	7 DAY $[Cl^-]/[OH^-]$	36 DAY $[Cl^-]/[OH^-]$	101 DAY $[Cl^-]/[OH^-]$
MK501					
0	0.1	0.19	0.04	0.02	0.02
0	0.4	1.11	0.20	0.14	0.13
0	1.0	3.35	0.49	0.51	0.41
10	0.1	0.11	0.11	0.04	0.03
10	0.4	0.63	0.36	0.17	0.19
10	1.0	1.68	0.48	0.44	0.43
20	0.1	0.11	0.06	0.06	0.06
20	0.4	0.40	0.21	0.27	0.27
20	1.0	1.26	0.46	0.57	0.56
MK505					
10	1.0	2.22	0.35	0.42	0.38
20	1.0	1.34	0.47	0.50	0.52

associated with a given dosage of chloride as a mix contaminant in the pastes containing 0, 10 or 20% of metakaolin. This is in marked contrast to the behaviour reported previously for certain silica fume cement pastes (18), where it was found that the inclusion of 1% chloride (by weight of total solids) in blended cement pastes containing 0, 10, 20 or 30% of silica fume gave rise to values of $[Cl^-]/[OH^-]$ in the respective pore solutions of 0.57, 2.8, 17.0 and 240.0.

Conclusions

Incorporation of metakaolin, as a partial cement replacement, into OPC pastes causes substantial changes in the chemical composition of the pore solution phase of the hydrated material. Significant reductions in the pH value of the pore solutions have been observed when 10 or 20% of metakaolin is blended with OPC of moderate alkali content (0.63% equivalent Na_2O). This consequence of the pozzolanic reactivity of metakaolin is considered to be relevant to the ability of metakaolin-blended cements to reduce the risk of expansive alkali-aggregate reaction in concrete but to have very little direct effect on the stability of the passive film that provides corrosion protection to embedded steel.

Blended cement pastes containing 10 or 20% of metakaolin have also been found to exhibit higher capacities than plain OPC pastes to bind chloride ions which are introduced by contamination of the mix water with sodium chloride. This effect counteracts the reduction in pH and results in $[Cl^-]/[OH^-]$ ratios in the pore solution phase, which are similar for OPC and metakaolin-blended cement pastes at the same dosages of sodium chloride. Thus the risks of chloride-induced corrosion of embedded steel are expected to be affected relatively little by the inclusion of up to 20% metakaolin in OPC-blended cement concretes.

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