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Microstructure and Phase Assemblage of Low-Clinker Cements during Early Stages of Carbonation

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Abstract

This study investigates the effects of carbonation following short curing periods (72 hours) on CEMI and composite cement systems (30% PFA, 30% & 60% GGBS). Modifications in carbonation behaviour were observed compared to ‘idealised’/28 day lab cured samples. Following 72 hours curing, consumption of $Ca(OH)_2$, via carbonation, was subsequently followed by decalcification of C-S-H, with notable changes in the C-S-H phase only occurring once Portlandite was completely depleted. Both calcium and aluminium were removed from the C-(A)-S-H phase as a result of exposure to ambient [CO_2], and at early stages of carbonation $CaCO_3$ microcrystals were observed in Op regions only. The carbonate species formed, and the rate and extent of carbonation, was reliant on the replacement material and level, as well as the degree of hydration.

1. Introduction

Carbonation of cement materials has been extensively studied, however these studies focus on fully hydrated/28 day cured systems, and predictions used for service life design rely upon models established for PC systems. Although the slower rates of reaction exhibited in composite cement materials are well understood, further knowledge is required about the early age reaction kinetics of both the PC and the SCM. This becomes of greater importance when the early removal of formwork is considered, potentially exposing a porous microstructure with a low degree of hydration which will be susceptible to attack from corrosive species.

The reduced $Ca(OH)_2$ content, characteristically exhibited by composite cement materials, presents further limitations when carbonation induced corrosion is considered. A decrease in the main alkalinity buffer will affect the carbonation resistance of the system, lowering of the pH allowing carbonation to occur at a greater rate and to a more extensive degree.

This study aims to investigate both the effect of carbonation on immature low-clinker binders, in terms of the development and changes in the phase assemblage and the microstructure, as well as the differences in carbonation behaviour between these systems and conventional carbonation studies.

2. Experimental

Four paste systems (CEMI, and CEMI with replacement by 30% PFA, 30% & 60% GGBS) at a w/b ratio of 0.57 were investigated. A CEM I 52.5R cement (free from limestone) was used, and replacement was by volume. Following preliminary work, and to mimic procedures commonly followed in practice, a curing length/t_0 value of 72 hours was selected. Samples were cast and sealed in small plastic vials and rotated for 72 hours in a temperature controlled laboratory (22 +/-2^{o}C) before being cut to a thickness of 0.5mm and subjected to conditioning at either ambient conditions (300-450ppm CO_2, approx. 24^{o}C) or in a CO_2 free environment. All samples were conditioned at a 72.6% relative humidity (RH) for up to 60 days. In order to study the effects of carbonation on the phase assemblage and microstructure only, very thin samples (0.5mm) were used, allowing the impact on the reaction kinetics to be investigated separately from effects on both the porosity and the transport properties.

Simultaneous Thermal Analysis (STA) data was collected using a Stanton Redcroft Simultaneous Thermal Analyser STA 780, under nitrogen, heating to 1100°C at a rate of 10°C/min. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) data was collected using a Thermo Scientific Nicolet Is10 spectrometer, fitted with a Thermo Scientific Smart Diamond ATR sampling accessory, over a wavenumber range of 0–4000cm^{-1}. TEM images were collected on Ar ion-beam milled samples using a FEI Tecnai TF20 FEG TEM.

3. Results and discussion

STA and ATR-FTIR data were collected for all the samples exposed to ambient CO_2. A large increase in carbonate content was clear in all the systems, corresponding to the complete, or nearly complete, consumption of $Ca(OH)_2$. This was evident in both the $Ca(OH)_2$ and $CaCO_3$ contents calculated from STA data, as well as the disappearance of the Portlandite peak (3643cm^{-1}) in the ATR-FTIR spectra. In addition to this, the depletion of $Ca(OH)_2$ coincided with a shift in the silicate band in the ATR-FTIR data, as well as a notable decrease in the $CaCO_3$ decomposition temperature in the TGA plots. Both observations indicate carbonation of C-S-H has begun, and that it begins only once no more $Ca(OH)_2$ is available. Firstly the shift to a higher wavenumber of the silicate band in the ATR-FTIR spectra suggest decalcification of the C-S-H phase, and the accompanying drop in carbonate decomposition temperature implies a much less crystalline carbonate species is being produced. It is believed that carbonates formed due to C-S-H carbonation are poorly crystalline, metastable forms of $CaCO_3$, and therefore decompose at a lower temperature than crystalline polymorphs, such as those produced from carbonation of $Ca(OH)_2$.

The loss of buffering capacity in the system allows carbonation to occur at a much faster rate and to a much greater extent. This behaviour was observed at a much earlier exposure age in the composite systems (between 2-4 days at 30% replacement, and 1-2 days at 60% replacement) compared with the CEMI sample (between 4-7 days). The more rapid rate of carbonation experienced by the composite systems is most likely further amplified by their limited degree of hydration, diffusion of CO_2 being aided by an underdeveloped microstructure.

TEM-EDX data revealed reaction of both the PFA and the GGBS had occurred in the 30% replacement systems, however the reaction of the slag was greater compared to the fly ash, agreeing with previous work reported in the literature (Fraay et al., 1989, Deschner et al. 2012, Escalante et al. 2001).

Table 1. Mean Ca/Si and Al/Si ratios for C-S-H for carbonated and non-carbonated systems at 7 days exposure (CEMI) and 4 days exposure (30% PFA & 30% GGBS)

	Ca/Si						Al/Si					
	0% [CO_2]			ambient [CO_2]			0% [CO_2]			ambient [CO_2]		
	N	Mean	S.D.	N	Mean	S.D.	N	Mean	S.D.	N	Mean	S.D.
CEMI	40	1.70	0.18		-	-	-	0.11 (Op) / 0.07* (Ip)	-	-	-	-
30% PFA	44	1.55	0.10	16.00	0.86 (Op)	0.14	25	0.13 (Op)	0.05	16	0.09 (Ip)	0.02
30% GGBS	75	1.39	0.20	35.00	0.57	0.07	75	0.16 (Op) / 0.11* (Ip)	-	15	0.10 (Op)	0.03

N = number of analyses, S.D. = standard deviation, Op = outer product C-S-H, Ip = inner product C-S-H

* Determined from regression analysis of Al/Si-Mg/Si plots at Mg/Si = 0

Table 1 displays the Ca/Si ratios of the non-carbonated systems, the decrease in comparison to the CEMI sample confirming reaction of the replacement materials after 72 hours curing. Values are in good agreement with other studies (Richardson, 2000, Taylor et al., 2010, Girao et al., 2010). Decalcification and dealumination of the C-(A)-S-H phase was observed by a reduction in both the Ca/Si and Al/Si ratios of the samples upon exposure to CO_2 (Table 1).

TEM micorgraphs showed coarsening of the Op C-S-H as a result of carbonation, further reinforcing decalcification of C-S-H. $CaCO_3$ microcrystals were observed in Op regions only, forming on Op C-S-H fibrils. Figure 1 shows a TEM micrograph for the carbonated PFA system at an exposure age of 4 days, $CaCO_3$ microcrystals observed in Op regions have been circled in white. However, TEM-EDX data showed a decrease in the Ca/Si ratio of both Op and Ip regions. Groves (Groves et al. 1990) attributed similar behaviour to carbonation shrinkage, Ca^{2+} cations migrating from Ip to Op regions as a result of a concentration gradient.

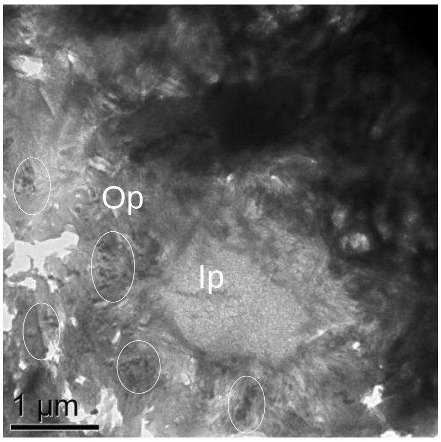

Figure 1. TEM micrograph for 30% PFA sample after 4 days exposure to ambient [CO_2]

4. Conclusions

Following 72 hours curing, more extensive carbonation was evident in the composite systems, behaviour attributed to a more porous material with a less developed microstructure.

A notable increase in carbonation was observed as $Ca(OH)_2$ was completely consumed, the loss of buffering capacity allowing carbonation to occur more rapidly, and occurred at an earlier age with increasing levels of replacement.

TEM-EDX analyses revealed both decalcification and dealumination of the C-(A)-S-H phase in the composite materials and TEM micrographs revealed coarsening of the Op region, with $CaCO_3$ microcrystals forming on Op C-S-H fibrils only. The decrease in Ca/Si ratio of the Ip regions was therefore attributed to the migration of Ca^{2+} cations, driven by a concentration gradient.

5. Acknowledgements

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