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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 behavior were observed compared to 'idealised'/28 day lab cured samples and accelerated carbonation testing. Furthermore, the rate and extent of carbonation and the nature of the carbonate species formed is dependent on the level of replacement, the replacement material and the degree of hydration.

1. INTRODUCTION

Pulverised Fuel Ash (PFA) and Ground Granulated Blast Furnace Slag (GGBS) are industrial by-products commonly used as SCMs. Though the reduced rate of hydration is well established, both the PC and the SCM will hydrate simultaneously, yet there remains a lack of knowledge regarding the early age kinetics of the reactions taking place. This becomes of great importance should formwork be removed too soon where the reliance on models established for PC systems may no longer be suitable. Under such conditions, hydration will be very much incomplete, with previous research indicating minor or no reaction of PFA over the first 7 days [1,2] and only slightly faster reaction rates for GGBS[3]. In both cases the result will be an underdeveloped and exposed microstructure, possibly susceptible to ingress from aggressive species.

Further to this, the expected retardation of the rate of CO_2 ingress typically observed in PC systems is as a result of densification of the microstructure. This, however, is not concurrent with the behaviour exhibited in high replacement SCM cements, which are adversely affected by a coarser microstructure and greater porosity upon carbonation.

This project has examined the early stage carbonation behaviour of immature low-clinker binders. The work will attempt to examine differences between these systems and conventional studies on mature systems.

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. This allowed the systems to develop enough strength so as to allow sample preparation and conditioning, while still representing the short curing period typically employed in practice.

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 (300-400ppm 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 14 days. Characterisation was performed on the samples at t_0, 1, 2, 4, 7 & 14 days.

Simultaneous Thermal Analysis (STA) data was collected using a Stanton Redcroft Simultaneous Thermal Analyser STA 780, under nitrogen, heating to 1100^{o}C at a rate of 10^{o}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 wave number 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

ATR-FTIR data were collected for all samples exposed to ambient CO_2. Figure 1 displays the characteristic ATR-FTIR absorbance band for carbonates between 1400 - 1500cm^{-1} collected for the 30% PFA system. Exposure to CO_2 led to an increase in $CaCO_3$ content. Furthermore a sizeable increase in carbonate content was observed between 2 and 4 days CO_2 exposure. Considering the normalised spectra for the silicate band and the $Ca(OH)_2$ peak (Figure 2), this considerable increase in carbonate content coincides with both the complete consumption of $Ca(OH)_2$, as demonstrated in Figure 2(b), and the decalcification of C-S-H, demonstrated by a shift in the silicate band (Figure 2(a)). This loss of buffering capacity allows carbonation to progress much more rapidly within the sample, and it appears that carbonation of C-S-H begins only once there is no more $Ca(OH)_2$ available.

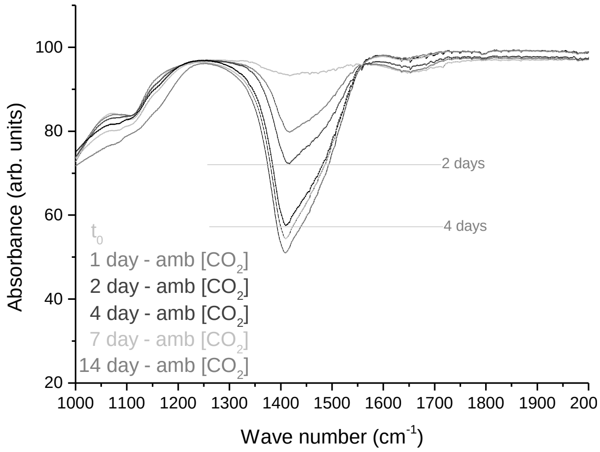

Figure 1. ATR-FTIR data for 30% PFA showing $CaCO_3$ content between 1000 – 2000cm^{-1}

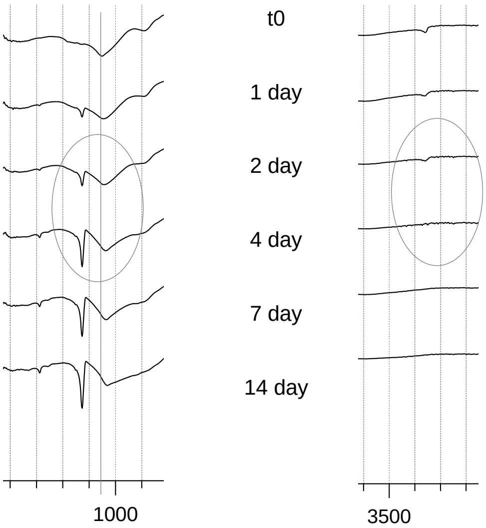

Figure 2. Normalised ATR-FTIR spectra for 30% PFA for (a) silicate bands and (b) $Ca(OH)_2$ peak (3643cm^{-1})

Similar behaviour was observed for all samples, but at different lengths of exposure. For the CEMI system this occurred between 4 and 7 days, then between 2 and 4 days for the 30% GGBS system and 1-2 days for the 60% GGBS system. The lower initial $Ca(OH)_2$ content in the composite blends resulted in a loss of buffering capacity at an earlier age compared with CEMI systems, behaviour exacerbated with increasing levels of replacement.

Table 1 displays the $Ca(OH)_2$ and $CaCO_3$ contents calculated from the STA data. A large increase in carbonate content was seen with the entire, or almost nearly entire, consumption of $Ca(OH)_2$, consistent with the ATR-FTIR data. Furthermore, faster more extensive carbonation was observed for both composite systems at 30% replacement compared to the CEMI sample. This highlights the more adverse effect of improper curing on composite cement materials. Composite materials, with slower rates of hydration, subjected to curing lengths of only a few days will exhibit open and underdeveloped microstructures, in which carbonation rate will occur much more rapidly. This behaviour between ‘idealised’/28 day lab cured samples and a more realistic curing length emphasises the need for updated carbonation models and approaches.

Table 1. Calculated $Ca(OH)_2$ and $CaCO_3$ contents from TGA data

	Ca(OH)2 content (%)	CaCO3 content (%)
CEMI		
t0	17.69	2.59
1 day amb [CO2]	16.51	4.12
2 day amb [CO2]	15.09	7.74
4 day amb [CO2]	8.65	18.79
7 day amb [CO2]	1.74	33.88
14 day amb [CO2]	0.00	47.49
7 day 0% [CO2]	17.99	0.00
14 day 0% [CO2]	18.82	0.00
30% PFA		
t0	13.97	1.66
1 day amb [CO2]	11.35	8.59
2 day amb [CO2]	8.56	16.37
4 day amb [CO2]	0.00	37.67
7 day amb [CO2]	0.00	41.59
14 day amb [CO2]	0.00	51.37
7 day 0% [CO2]	14.46	1.18
14 day 0% [CO2]	14.16	3.81
30% GGBS		
t0	12.80	1.63
1 day amb [CO2]	11.03	6.80
2 day amb [CO2]	9.13	12.25
4 day amb [CO2]	2.52	28.74
7 day amb [CO2]	0.00	37.65
14 day amb [CO2]	0.00	47.46
7 day 0% [CO2]	12.65	0.00
14 day 0% [CO2]	13.12	1.62
60% GGBS		
t0	8.15	1.48
1 day amb [CO2]	5.31	12.36
2 day amb [CO2]	0.00	25.44
4 day amb [CO2]	0.00	26.43
7 day amb [CO2]	0.00	30.82
14 day amb [CO2]	0.00	32.83
7 day 0% [CO2]	6.89	0.00
14 day 0% [CO2]	-	-

Furthermore the extent of carbonation was affected by both the replacement material and level. Although similar carbonation behaviour was observed for the materials with equal replacement levels, carbonation occurred to a greater degree, and at a faster rate, for the PFA system compared with the GGBS system. This is a reflection of the PFA's slower reaction rate, effects magnified with decreasing curing length. Carbonation is initially much faster in the 60% GGBS sample, with a vast increase in carbonate content between t_0 and 2 days (Table 1), however a plateau was reached at 4 days, with minimal subsequent carbonation, data supported by the ATR-FTIR data. This suggests that, with the limited degree of hydration likely in a high replacement system at an early age, all potential carbonatable hydration phases have been carbonated by this time.

STA and ATR-FTIR data showed that the samples conditioned in a CO_2 free environment indicated no continued hydration at 72.6% RH. Ho et. al[4] demonstrated that there is minimal hydration at RH levels below 80%.

There are typically 3 decomposition modes associated with carbonation; mode I (780° – 990°C), mode II (680° – 780°C) and mode III (550° – 680°C). The higher decomposition modes, mode I & II, are responsible for the crystalline polymorphs of $CaCO_3$ (calcite, vaterite and aragonite), with mode I being principally attributed to very well crystallised $CaCO_3$, i.e. calcite[5]. Mode III is believed to be associated with amorphous $CaCO_3$.

DTA data showed an increase in decomposition temperature with prolonged carbonation for all the samples, indicating the presence of better structured/crystallised $CaCO_3$, or calcite, as carbonation progresses. However, as the measurable level of carbonates increases, the mass loss associated with $CaCO_3$ drops to a lower temperature. This behaviour coincides with both the loss of $Ca(OH)_2$ and the significant increase in carbonate content as previously indicated by the ATR-FTIR and TGA data. This strongly indicates carbonation via decalcification of C-S-H, further corroborating the shift in silicate bands observed in the infrared spectra. It is considered that the carbonation of C-S-H corresponds to the formation of poorly crystallised and metastable forms of $CaCO_3$, explaining the shift to a lower decomposition mode exhibited here. Villain et. al[6] suggested the dissociation of stable $CaCO_3$ (calcite), attributed to $Ca(OH)_2$ carbonation, occurred between 650° – 950°C, while unstable forms of vaterite and aragonite resulting from C-S-H carbonation dissociated between 530° – 650°C for highly hydrated (cured for 3 months) mortar samples subjected to accelerated carbonation. Accelerated carbonation has been extensively researched, reporting the simultaneous carbonation of $Ca(OH)_2$ and C-S-H, with a much faster reaction rate of $Ca(OH)_2$ initially observed, the rate decreasing as carbonate phases were produced at the crystal surface[7, 8]. The results presented here indicate modifications in the carbonation mechanism between accelerated and natural carbonation, as well as between mature and immature specimens. Moreover carbonation at ambient CO_2 concentrations for samples cured for 72 hours implies that it is the $Ca(OH)_2$ phase initially involved in the carbonation reaction, and once consumed carbonation of C-S-H begins.

Table 2. Temperature at which mass loss due to $CaCO_3$ decomposition commenced.

	Temperature CaCO3 decomposition begins	
	Age (days)	(oC)
CEMI	t0	550
	1 day	560
	2 day	550
	4 day	530
	7 day	**455**
	14 day	400
30% PFA	t0	550
	1 day	540
	2 day	530
	4 day	**410**
	7 day	400
	14 day	400
30% GGBS	t0	580
	1 day	540
	2 day	530
	4 day	**450**
	7 day	450
	14 day	390
60% GGBS	t0	550
	1 day	520
	2 day	**310**
	4 day	350
	7 day	300
	14 day	230

Figure 3 shows TEM images obtained from a 72 hour old 30% GGBS paste after exposure for 4 days at both (a) 0% CO_2 and (b) ambient CO_2 concentrations. The foil like morphology of the outer product (OP) C-S-H, characteristic of composite GGBS cements, is clear in both images, with some fine fibrillar inner product (IP) C-S-H also present in Figure 3(b). The images clearly highlight the effects of carbonation on the OP. The carbonated sample shows a coarsening of the OP C-S-H, compared to the non-carbonated sample, further reinforcing the carbonation of C-S-H at this age. There appears to be no change in the IP C-S-H due to carbonation.

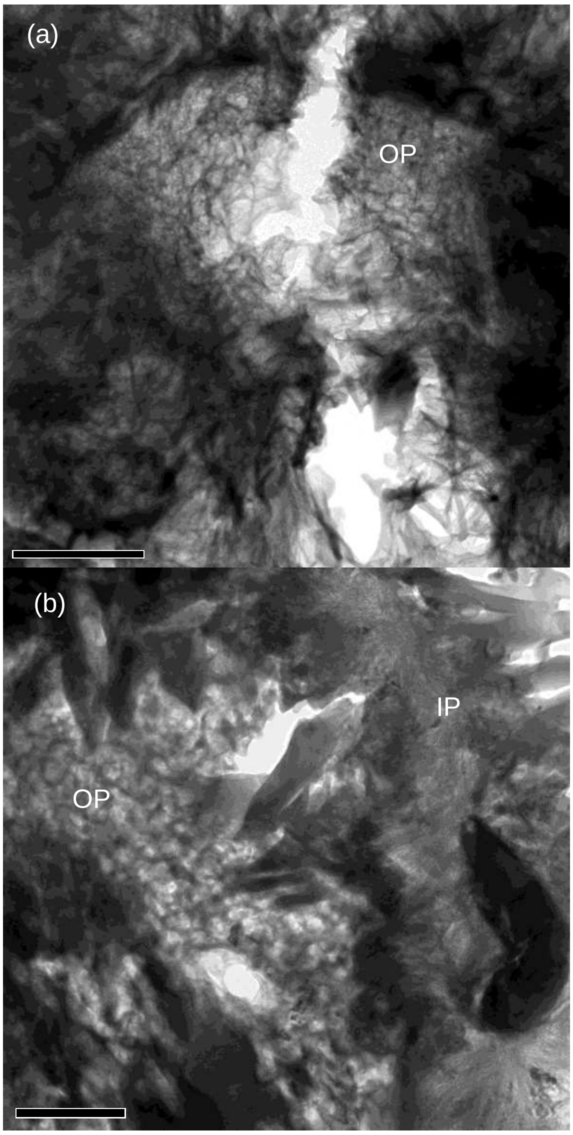

Figure 3. TEM images from an ion-milled 30% GGBS sample cured for 72 hours before being exposed to (a) 4 days at 72.6% RH, 0% [CO_2]; (b) 4 days at 72.6% RH, ambient [CO_2]

4. CONCLUSIONS

Carbonation of immature paste samples was followed by a range of characterisation techniques. There was no continued hydration and changes were due to carbonation only.

CEMI systems showed better carbonation resistance compared to composite systems 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. This coincided with C-S-H decalcification, confirmed by ATR-FTIR, TGA & TEM data. This occurred at an earlier age with increasing levels of replacement, believed to be a result of the already initially lower $Ca(OH)_2$ content typical of composite cement materials.

DTA data showed a shift in decomposition temperature as carbonation initially progressed, indicating the formation of better structured/well crystallised $CaCO_3$ with increasing carbonate content. However, as carbonation continued, a drop in $CaCO_3$ decomposition temperature was observed, coinciding with the consumption of $Ca(OH)_2$. This lower temperature also indicated $CaCO_3$ formation due to carbonation of C-S-H. Carbonation of $Ca(OH)_2$ and C-S-H did not occur simultaneously, decalcification of C-S-H only beginning once $Ca(OH)_2$ had been consumed.

TEM images verified carbonation of OP C-S-H. Carbonation appears to have affected the OP foil like hydrate phase only, a coarsening of the microstructure was clearly visible.

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