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

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ABSTRACT

Differences in carbonation behaviour of paste samples exposed to ambient CO_2 concentrations were investigated. Modifications in behaviour were observed between samples cured for short periods of time (72 hours) and those subjected to 'idealised' lab cured conditions (28days), as well as between CEMI and blended cement systems. Carbonation of AFm phases occurs very early, with decomposition of AFt only occurring after much longer exposure times, if at all. Although decalcification of C-S-H is evident when CH is present, it is once CH is no longer available that significant changes in the C-S-H structure are observed. The formation of carbonation products such as gypsum and silica gel were clear in blended systems after only 60 days exposure to ambient CO_2 concentrations and 72 hours curing.

1. INTRODUCTION

The use of blended cement systems in construction can be advantageous when it comes to durability aspects, however failure to acknowledge, and employ, correct curing guidelines by the early removal of formwork may cause problems with respect to material durability and strength gain. Predictions used for service life design rely upon models established for PC systems, but do not consider the slower rates of reaction of composite materials. Moreover, the reduced $Ca(OH)_2$ content, characteristically exhibited by blended cement materials, presents further limitations when carbonation induced corrosion is considered.
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, 28 day cured samples 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. In order to investigate the effect of curing on carbonation behaviour, two curing lengths/t_0 values were chosen: 72 hours and 28 days. 72 hours was selected, following preliminary work, as a more realistic curing period, to mimic procedures commonly followed in practice, whereas 28 days represents the recommended laboratory testing standard. Samples were cast and sealed in small plastic vials and rotated for 72 hours in a temperature controlled laboratory (22 +/-2°C) before being cut to a thickness of 0.5mm and subjected to conditioning at either ambient conditions (300-450ppm CO_2, approx. 24°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.

Carbonation depth was measured on 40 x 40 x 80mm mortar prism (made in accordance with the procedure outlined in BS EN 196-1:2005 - modified to correspond with the ratios studied in the paste samples (0.40 & 0.57). Samples were cured for either 72 hours or 28 days and then left to carbonate in ambient conditions in the laboratory (RH 50% +/- 10%, $[CO_2] \approx 450$ppm). Depth of carbonation was determined using a 1% phenolphthalein solution, the indicator was sprayed onto a freshly broken surface and 5 points along each of the four edges were measured.

Simultaneous Thermal Analysis (STA) data was collected using a Stanton Redcroft Simultaneous Thermal Analyser STA 780, under nitrogen, heating to 1000°C at a rate of 10°C/min. TEM images were collected on Ar ion-beam milled samples using a FEI Tecnai TF20 FEG TEM. ^{27}Al MAS NMR spectra were collected by the solid-state NMR service at Durham University. ^{27}Al spectra were collected at an operating frequency of 104.199MHz, and spin speeds of 12000 – 14000 Hz. A pulse duration of 1.0µs, 10ms acquisition time and 0.2s recycle time were used. UCS was determined using a Dennison Compressive Loading T42 B4 on an area of 40mm using machine manufactured steel plates of corresponding size.

3. RESULTS AND DISCUSSION

Carbonation of all the hydrate phases (CH, C-S-H, AFm & AFt) is evident in each of the systems following a curing period of 72 hours, apart from the CEMI samples in which ettringite remained unaffected up to the full length of exposure (60 days). Compete consumption of CH occurred in all systems, as observed in STA and ATR-FTIR data not shown here, and was observed to occur at earlier lengths of exposure with increasing levels of replacement. Although ^{29}Si MAS NMR spectra of the samples, again not shown here, confirmed decalcification of C-S-H in the presence of CH, indicated by a decrease in the Q^1 and corresponding increase in the Q^2 peak (Groves et al., 1991, Sevelsted and Skibsted, 2015) it is not until CH has been completely consumed that carbonation is allowed to progress much more rapidly. This is illustrated in Figure 1 for the 30% GGBS system, where consumption of CH reaches a plateau after 4 days (solid line with circles), indicating depletion of portlandite, while sizeable formation of $CaCO_3$ is clear (dashed line with circles) up to ages of 60 days. This suggests that once CH is no longer available, carbonation of C-S-H is allowed to progress much more rapidly, behaviour observed for all the systems. Thiery et al. 2007, also reported this behaviour, describing it as a rate determining stage which is controlled by the accessibility of the CH crystals. However, their study carbonated 8 month cured cylindrical prisms (⌀ = 3.2cm, h = 8cm) in a 50% CO_2 atmosphere, so although CH is initially carbonated much more quickly than C-S-H, it is the formation of $CaCO_3$ microcrystals at the crystal surfaces that inhibits further decomposition, allowing decalcification of C-S-H to proceed more vigorously. In this study, STA, XRD and ATR-FTIR all confirm it is complete consumption of CH, rather than inaccessibility of the crystals, that permits the rate of carbonation of C-S-H to increase. Groves et al. 1991, discussed the carbonation of C_3S pastes in both air and pure CO_2. Again, a much faster initial reaction rate of CH was observed, followed by a significant decrease and continuing reaction of the C-S-H phase for both CO_2 concentrations. Although, this was determined to be a result of coating of microcrystalline carbonate on the portlandite crystals in the pure CO_2 carbonated samples, there was no evidence to suggest this being the cause in the air carbonated specimens.

Figure 2 displays ^{27}AL MAS NMR spectra for the 30% GGBS system following curing for 72 hours. Figure 2(a) presents spectra for non-carbonated samples at exposure ages of 0 (t_0) and 60 days, the peaks at ≈ 9 and 13ppm are assigned to AFm and AFt respectively (Skibsted et al. 1993). Firstly, it is clear that no continued hydration of the aluminates occurs during sample conditioning at a RH of 72.6% (^{29}Si spectra also show no change in the C_3S and C_2S peak (Q^0 peak)), which is in agreement with other studies reporting no significant hydration below RH levels of 80% (Ho et al., 1989). The carbonated samples are shown in Figure 2(b) following 4 days (bottom) and 60 days exposure (top) to ambient CO_2 concentrations. What is clear is a large decrease in the peak attributed to AFm at early age, followed by the loss of the peak attributed to AFt at later ages. Decomposition of AFm is observed at very early ages in all of the systems, whereas ettringite carbonates only in the blended materials. This is further confirmed by XRD and DTA data which show loss of AFt and formation of gypsum from 14 days exposure for the systems with 30% replacement, and from 7 days for the 60% slag system. The effect of carbonation of the AFm phases can be seen clearly in the TEM micrograph displayed in Figure 3. The micrograph shows a heavily carbonated AFm region in the 30% GGBS system, in which the large AFm plates have visibly shrunk and split.

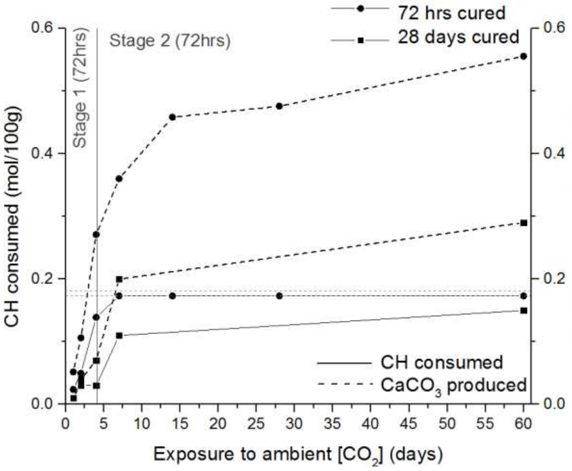

Figure 1. Consumption of CH versus production of $CaCO_3$ calculated from STA data for 30% GGBS cured for 72 hours and 28 days. Values are shown in mol/100g. Total amount of CH available at t_0: 72hrs = 0.17mol/100g, 28 days = 0.18 mol/100g (indicated by grey dashed lines).

Figure 1 gives a comparison of the two curing lengths in terms of the consumption of CH and the corresponding production of $CaCO_3$ (in mol/100g) for the 30% GGBS system. As with all the systems, CH is present much longer following 28 days curing, as indicated by the continuing consumption of CH on the graph. In the samples cured for just 72 hours, CH was completely consumed after 4 days exposure, whereas, a very small amount (2.5% (function of ignited mas)) of portlandite is still observed at 60 days exposure in the 28 cured system. It is also interesting to note that depletion of CH was observed from 14 days exposure in the remaining 3 system. When samples were subjected to curing for 72 hours, CH was seen to be consumed at 7, 4 and 2 days for 0%, 30% and 60% replacement levels respectively. Ideal curing conditions, however, indicate that the 30% slag system has the greatest resistance to carbonation, and a comparable performance, in terms of carbonate formation and loss of portlandite, for the CEMI, 30% PFA and 60% GGBS materials. This is likely an impact of the porosity, the refinement of the microstructure in slag cements resulting in reduced rates of diffusion (Richardson and Groves, 1992).

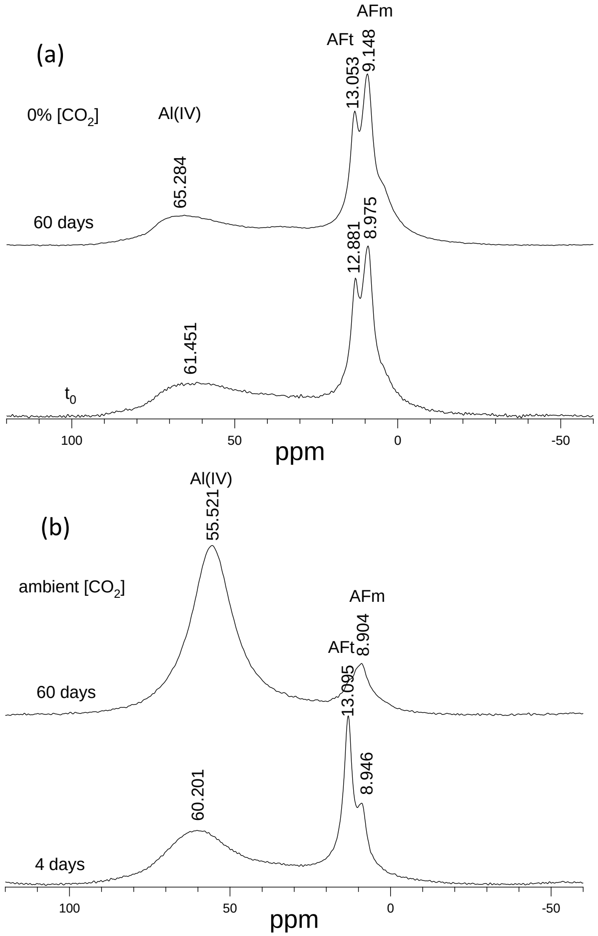

Figure 2. Single-pulse ^{27}AL MAS NMR spectra for 30% GGBS 0.57 (72hr) sample following exposure to (a) 0% [CO_2] for 0 (t_0) and 60 days (b) ambient [CO_2] for 4 and 60 days.

The buffering capacity of portlandite is clearly illustrated in Figure 1, demonstrating that although carbonation occurs when it is present, or available, (labelled as stage 1 for 72 hour cured samples), it is once it has been consumed, or can no longer be accessed, that carbonation of the other hydrate phases is allowed to proceed at a much more rapid rate (labelled as stage 2 for 72 hours cured samples). Further to this, the formation of gypsum in DTA and XRD data, indicating decomposition of AFt due to carbonation (Zhou and Glasser, 2000), occurs only in the blended systems following 72 hours curing, i.e. from 7 days for 60% GGBS and from 14 days for 30% PFA and 30% GGBS. The formation of gypsum as a result of carbonation is not observed in the CEMI or either slag system when cured for 28 days, however, it is clearly detected from 28 days in the PFA cement.

Although the presence of portlandite, or its accessibility, seems to govern the rate of carbonation, protecting more aggressive decalcification of C-S-H from occurring, the decomposition of ettringite seems to be dependent on the material and degree of hydration.

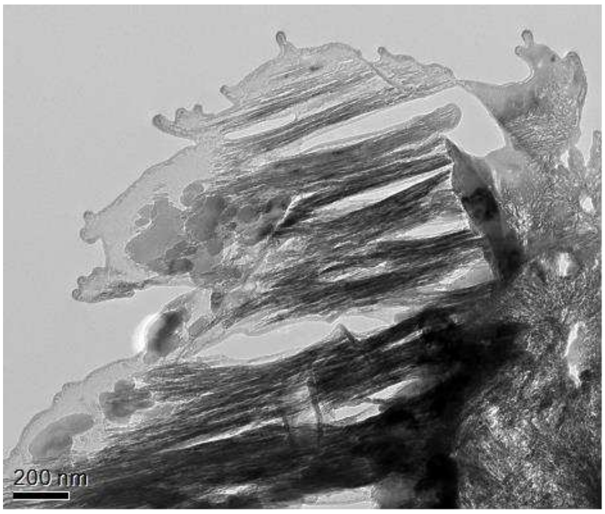

Figure 3. TEM micrograph showing carbonated AFm regions of 30% GGBS 0.57 (72hr) sample following exposure to ambient CO_2 concentrations for 60 days.

Carbonation depth data measured on mortar prisms (40 x 40 x 80mm) exposed to ambient CO_2 concentrations for 18 months (Figure 4), provides some insight into the effect of w/b ratio on carbonation resistance. Data for both curing lengths, as well as a lower w/b ratio (0.40) are given. It is initially apparent that the w/b ratio appears to be the controlling factor for ingress of CO_2, primarily in the CEMI and 30% replacement systems. At a w/b ratio of 0.57, carbonation depth is markedly higher for both lengths of curing, and this is amplified in the blended cements. The slag system, however, performs much better compared with the equivalent fly ash system, the slower reaction rate of PFA (Fraay et al., 1989 and Deschner et al., 2012) negatively affecting overall degree of hydration and total porosity. This is most striking for the 28 day cured PFA samples which show an extremely large carbonation depth, which has a greater mean value than that of the corresponding 60% slag system. The effect of curing is more apparent for the 60% GGBS system, where for both w/b ratios the difference in carbonation depth is much greater between the two curing lengths. Curing for 72 hours has a significant impact on the extent of carbonation ingress at both high and low water contents, emphasising the need for extended curing lengths at higher levels of substitution. Although durability standards provide some guidelines on the length of curing (BS EN 13670:2009 Execution of concrete Structures), these recommendations focus on the ratio of compressive strength development in the surface zone. In order to take into account the considerable effect replacement level, replacement material, w/b ratio and curing length have on material performance, and resistance to carbonation, updated guidelines that include information on these parameters are needed. One possibility could be to include standards for the selection of a w/b ratio, recommending maximum water contents to be used depending on intended level of replacement and replacement material.

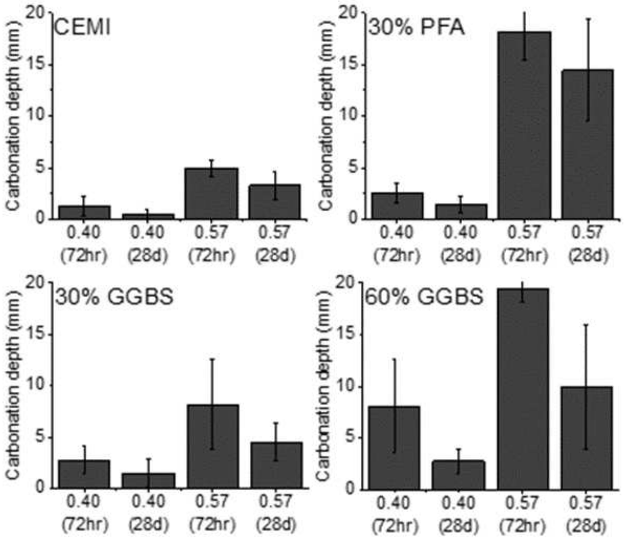

Figure 4. Carbonation depth of mortar samples exposed to ambient CO_2 concentrations for 18 months (measured using phenolphthalein indicator) comparing the effect of curing length (72hrs v 28d) and w/b ratio (0.40 v 0.57) on carbonation resistance.

4. CONCLUSIONS

Analysis of intrinsic carbonation rate on thin paste specimens:

Following 72 hours curing, a large increase in carbonate content was observed once CH had been consumed, the loss of buffering capacity allowing more rapid carbonation of C-S-H to occur.

Carbonation of all hydrate phases was evident, apart from the CEMI system in which AFt appeared to remain unaffected.

^{27}Al MAS NMR spectra indicated that carbonation of AFm occurred at very early ages in all the systems, while decomposition of AFt only occurred later in the blended systems only, i.e. from 7 and 14 days exposure for 60% and 30% levels of replacement respectively.

Following 28 days curing, carbonation is observed to occur at slower rate and to a lesser extent in all the materials. CH is present for much longer in all the systems, and a small amount is still present at 60 days exposure in the 30% slag system, whereas complete consumption is observed from 14 days exposure for the remaining 3 systems.

The presence, or accessibility, of CH prevents significant decalcification of the C-S-H.

The formation of gypsum, indicating decomposition of AFt as a result of carbonation, was only observed in the PFA system (28 days onwards), demonstrating the choice of material and degree of hydration has a large impact on the carbonation of the hydrate phases other than CH and C-S-H.

The effect of w/b ratio and curing length on carbonation depth of mortar samples:

For all the systems a significantly higher depth of carbonation is observed at the w/b ratio of 0.57 following both curing lengths, suggesting that the w/b ratio is a controlling factor.

The slag system performs notably better at the higher w/b ratio in comparison to the equivalent fly ash system.

At higher levels of replacement (60%) the effect of curing is more prominent, where extended curing greatly improves resistance to ingress of CO_2.

Durability standards for blended cement systems need to consider, and include, guidelines on the length of curing and w/b ratio selection depending on the intended level of replacement, and the replacement material.

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