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

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ABSTRACT

Increasing and widespread use of Supplementary Cementitious Materials (SCMs) in the cement industry has become common practice. However, such systems hydrate more gradually than pure Portland Cement (PC) systems, and though concrete standards include recommended modified curing lengths for more slowly hydrating systems, the premature removal of formwork risks exposing an underdeveloped microstructure that is vulnerable to ingress and attack from aggressive species. Design models established for Portland Cement systems are acceptable when low levels of replacement are used, but may be unsuitable if higher levels of replacement are used. In such systems an understanding of the complex relationship between composite cement hydration, drying of the sample surface and phase carbonation kinetics is imperative. The main objective of this project will be to develop an understanding of the changes and development of the early-stage morphology and phase assemblage of composite systems as a result of carbonation. Evolution of the morphology will be investigated using SEM and TEM, while changes in the phase assemblage will be analysed through XRD, NMR and TGA. Further complementary analysis using Raman and FTIR Spectroscopy will also be performed. It will be key to establish how the systems evolve over time in these very early stages as a result of slower hydration, desiccation and phase carbonation.

1. INTRODUCTION

Increasing and widespread use of Supplementary Cementitious Materials (SCMs) in the cement industry has become common practice. The use of these composite cements is advantageous in both environmental and engineering aspects, acknowledging the ever rising pressures to further reduce carbon production associated with cement manufacture. It has been well established that utilising SCMs leads to significant reductions in associated CO₂ emissions in addition to notable improvements in terms of durability through enhancement of the cement microstructure; however, development of superior technological properties is reliant on adequate curing. Composite cements exhibit reduced rates of hydration, making them dependent upon extended periods of moist curing. The need for sufficient curing procedures is recognised in concrete standards where adjusted curing periods and regimes are recommended in relation to the development of particular properties within the surface region (BS EN 13670:2009, Execution of Concrete Structures). It is also demonstrated extensively throughout the literature (Ramezani-pour and Malhotra, 1995, Poon et al., 1997, Cakir and Aköz, 2008), in which it has been highlighted that composite cement materials are more adversely affected by poor and inadequate curing methods than traditional CEMI systems. Failure to adhere to these prolonged curing guidelines by early removal of formwork in

construction practice may cause fundamental problems with respect to both durability and strength gain. Information regarding material performance is needed, especially at these very early ages.

Yielded from the manufacture of coal and steel, Pulverised Fuel Ash (PFA) and Ground Granulated Blast Furnace Slag (GGBS) are industrial waste products and have become the common convention for use as cement replacement materials. Information regarding their durability as SCMs is therefore of great importance and has become a main focus of cement and concrete related research. Though it is well established that a reduced rate of hydration is observed with both materials, owing to their pozzolanic and latent hydraulic properties, both the PC and the SCM will hydrate simultaneously, yet there is still a significant lack of knowledge regarding the early age kinetics of the reactions taking place. This becomes of great importance when considering the early removal of formwork in practice 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 up to hydration periods of 7 days (Fraay et al., 1989, Deschner et al., 2012) and only slightly faster reaction rates for GGBS (Escalante et al., 2001). In both cases the result will be an underdeveloped and exposed microstructure, vulnerable to ingress and attack from aggressive species. A

comprehensive understanding of the complex relationship between slower hydration, drying of the sample surface and phase carbonation kinetics is imperative. Current models derived from idealistic, i.e. fully hydrated and non-carbonated, materials, are ineffective for durability predictions. In addition to this, the existing models do not consider the effects that insufficient curing and phase carbonation have on the phase assemblage composition, development of the microstructure and the subsequent consequences for the transport properties. New models relating these factors are crucial for the further development and understanding of service life design.

Furthermore, the reduced Ca(OH)_2 content characteristic of composite cements, or low clinker binders, presents additional limitations when considering resistance to carbonation induced corrosion (Hewlett, 2003). The decrease of Ca(OH)_2 , the main alkalinity buffer, resulting in a reduced pH, allows carbonation to occur at elevated rates and to greater extents, behaviour which is expected to become more pronounced with increasing levels of replacement. 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.

The main objective of this project will be to develop an understanding of the changes and development of the early stage morphology and phase assemblage of composite systems as a result of carbonation. It will be key to establish how the systems evolve over time in these very early ages as a result of the interplay of slower hydration, desiccation and phase carbonation.

2. EXPERIMENTAL WORK

The principal focus of the project is to investigate the changes in morphology and phase assemblage of these very early age composite systems as a result of carbonation. The evolution of the microstructure and changes in the phases present will initially be established as a function of time and relative humidity, enabling changes due to continued hydration to be differentiated from those due to simultaneous hydration and carbonation. Microstructural characterisation will be performed using SEM and TEM. XRD, TGA and NMR analysis will then determine the phase assemblage of each sample. Samples will then be exposed to ambient CO_2 levels and analysed using the same techniques above, establishing the changes resulting from carbonation of the systems.

Table 1 displays the samples that will undergo detailed analysis. In order to mimic the conditions

whereby formwork is removed after 24 hours, samples will typically be cured for short periods, i.e. 1-3 days. This should provide samples of sufficient robustness such that they can be prepared for analysis and still imitate the procedure currently followed in practice. Preliminary testing has shown that this should be less than 48 hours for all the samples.

Table 1. Samples for detailed analysis

	w/b	w/c	w/b	w/c
CEMI	0.40	0.40	0.57	0.57
CEMI/30% PFA	0.40	0.57	0.57	0.81
CEMI/30% GGBS	0.40	0.57	0.57	0.81
CEMI/60% GGBS	0.40	1.00	0.57	1.43

*it should be noted that CEMI samples will be made using a CEM 52.5 N and all samples involving partial replacement by other materials will use a CEM 52.5 R – The use of a cement with a higher early age strength (CEM 52.5R) for the samples involving replacement will allow similar early strength and performance development between the reference CEMI systems and the composite samples.

3. PRELIMINARY EXPERIMENTAL RESULTS

Preliminary results obtained indicate that the onset of carbonation is evident within the first few hours. Figure 1 and Table 1 display Thermal Analysis data of cement paste samples with 35% replacement of PFA and GGBS (CEMI/35% PFA, CEMI/35% GGBS). Samples were cured for a period of 24 hours before being crushed and allowed to carbonate in the laboratory up to a period of 4 hours.

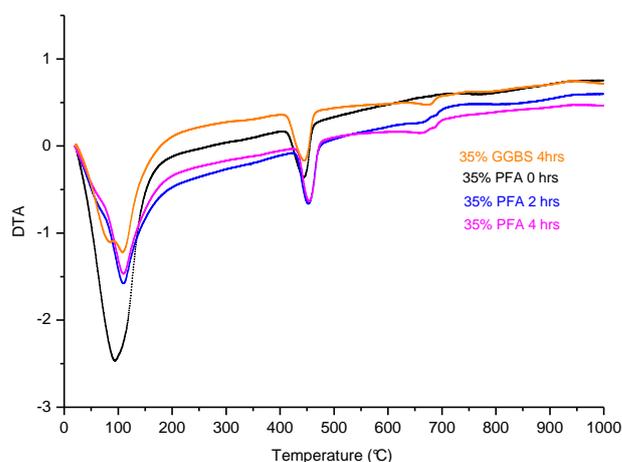


Figure 1. Differential Thermal Analysis (DTA) plot of lab carbonated samples, 35% PFA (w/b;0.55) and 35% GGBS (w/b;0.55), at 0, 2 and 4 hours.

Figure 1 illustrates a small but gradual increase of CaCO_3 with time for the PFA sample at around 650 - 700 °C, this transformation is indicated by the slightly pronounced change in differential temperature in this range. Table 2 further corroborates this behaviour by displaying increasing calculated amounts of CaCO_3 in the sample with increasing carbonation time.

Table 2. Calculated CaCO_3 contents of lab carbonated samples from Thermogravimetric data, 35% PFA (w/b;0.55) and 35% GGBS (w/b;0.55), at 0, 2 and 4 hours.

	Carbonation length (hrs)	Calculated CaCO ₃ (%)
CEMI/35% PFA (0.55)	0	0
CEMI/35% PFA (0.55)	2	4.5
CEMI/35% PFA (0.55)	4	6.8
CEMI/35% GGBS (0.55)	4	5.4

Meanwhile, XRD data, displayed in Figure 2, suggests that there is no change in CaCO₃ content. This infers that observed CaCO₃ in the Thermal Analysis data is present in its amorphous form, as has been observed previously during very early stage carbonation, albeit on synthetic samples (Black et al., 2007). It was reported that with time the amorphous CaCO₃ detected crystallised to form the polymorphs vaterite or aragonite. It follows, for this project, that in order to accurately investigate the carbonation at such early stages, a variety of techniques will be required and will include Thermal Analysis, XRD and Raman Spectroscopy.

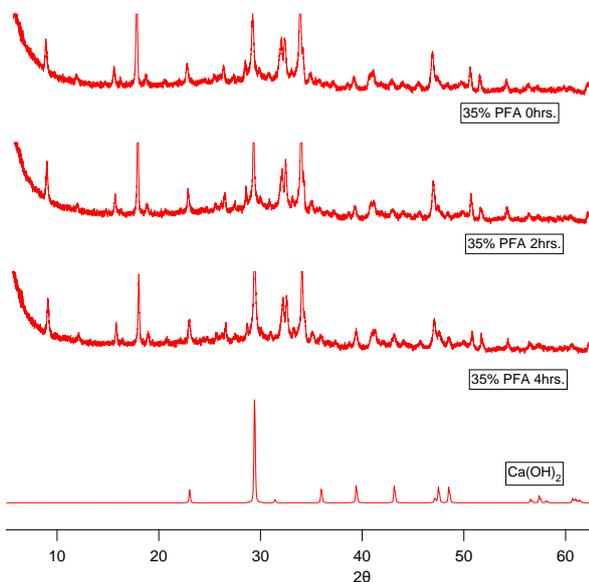


Figure 2. XRD traces of lab carbonated samples, 35% PFA (w/b:0.55), at 0, 2 and 4 hours.

It is evident that carbonation begins within the first few hours of exposure to ambient conditions, and it will therefore be important to characterise samples on very short timescales in order to establish the effects of carbonation coupled with both sample drying and continued hydration.

Furthermore, levels of replacement, type of replacement material and water content will additionally affect the mechanism of carbonation. Potential differences in behaviour may be gleaned from Figure 1 and Table 2. As stated previously, it is known that PFA will not have hydrated in a 24 hour old paste, while GGBS will have undergone a small degree of hydration. This may explain the subtle differences between the PFA and GGBS samples subjected to an equivalent carbonation length of 4 hours and at equal levels of

replacement (35%). This difference is, however, very minor and the results are only an indication of the approach and manner of the project.

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