

# Properties of Cementitious Composites Produced using Supercritical Carbon Dioxide

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## 1. Introduction

Supercritical fluids close to their critical point have density and thus dissolving power comparable to that of a liquid, are much more compressible than dilute gas, and have transport properties intermediate between those of gases and liquids [1]. In the case of carbon dioxide, the fluid reaches the critical point at a pressure of 73.8 bar and a temperature of 31.1°C. Above these temperature and pressure, the fluid enters the supercritical state [1]. Carbon dioxide in this form – scCO<sub>2</sub> – has the reactive and dissolving power of a liquid, but can access the small pores like a gas.

The effect of scCO<sub>2</sub> on the structure of cements was initially investigated by the oil industry [2] but its use as a treatment to improve the properties of cementitious composites was initiated by Jones in the late 1990s [3]. The main reactions involved in the carbonation of hydrated cement result in the decalcification of portlandite and calcium silicate hydrate (C-S-H) gel, with consequent crystallisation of calcium carbonate. Like natural carbonation, the process reduces the hydroxide concentrations in the pore solution, lowers the pH and alters the mechanical properties and microstructure of the cementitious materials [4]. It has been shown that carbonation of cement-based materials by the supercritical process is greatly accelerated (from years to hours) in comparison with natural carbonation. This is due to the significant rise of CO<sub>2</sub> solubility in water with the increase in pressure, and to the relative ease of penetration and diffusion of the supercritical carbon dioxide into the cement paste pore network [4].

More recent studies have demonstrated that scCO<sub>2</sub> treatment can significantly enhance the matrix strength, fibre-matrix bond, durability and dimensional stability of cement based composites, especially glass-fibre reinforced concrete [5-8]. The improvements in durability were associated with the reduction in the alkalinity of the pore solution, and substantial conversion of calcium hydroxide and anhydrous materials to calcium carbonate and silica gel. Improvements in mechanical properties and dimensional stability were related to significant reductions in total porosity (due to deposition within the pore network of the calcium carbonate formed by the process) and modification of the micro-pore structure and size distribution within the C-S-H gel phase [4-9]. These investigations have also established some of the parameters that govern the efficacy of scCO<sub>2</sub> treatment, particularly that the moisture content of components immediately prior to treatment is crucial to the degree of property enhancement, the amount of calcium hydroxide, anhydrous material and C-S-H gel remaining after carbonation, and the resultant pore structure [9].

This project is aimed at investigating the potential for using a supercritical carbonation process in combination with other processing techniques such as

compression moulding to fabricate a new class of ceramic composites from a variety of calcium-based precursor materials, including lime and cement.

In this investigation, compression moulding as used for mass-produced polymer components, was used to fabricate green forms (having 'sand-castle' strength and able to carry their self weight while avoiding structural failure), which were then hardened by treatment with supercritical CO<sub>2</sub>. The effect of the treatment on the microstructure, solid phase assemblage and engineering properties of specimens was then investigated using methods including X-ray diffraction (XRD), Scanning electron microscopy (SEM), thin section petrography (TSP) and 4-point bending tests.

Here, preliminary results reporting the effect of variations in mix design such as binder composition, aggregate content and type, and influence of water curing on the degree of carbonation, strength and microstructure of samples are reported.

## 2. Materials and Methods

170mm long green samples were manufactured using a compression moulding technique combined with vacuum dewatering. The green specimens had trapezoidal cross sectional shape with 22/34 mm wide × 17 mm depth. This shape was chosen for ease of demoulding and was settled upon after many trials and alterations. The tool used to mould the samples was fixed to a thermoset compression moulding (DASSETT) machine and samples were subjected to 19 MPa pressure (466kN load) from the machine for duration of 1 minute. Excess water was squeezed out of the samples was removed by vacuum through filter sheets and holes in the tool.

Binders used were combinations of hydrated lime [L] and ordinary Portland cement [C]. Aggregates [Agg] were combinations of normal silica sand [S], crushed limestone (2.36 mm to dust fraction) [CL] and silica aggregate (SA) engineered to have the same particle size distribution as CL. SA was used as a replacement to CL in certain mixes to study the effect of crushed limestone in the mix and investigate whether any physico-chemical effects over and above simple packing effects were significant with regard to flexural strength.

**Table 1. Curing regimes for control and treated samples produced by optimum mix design.**

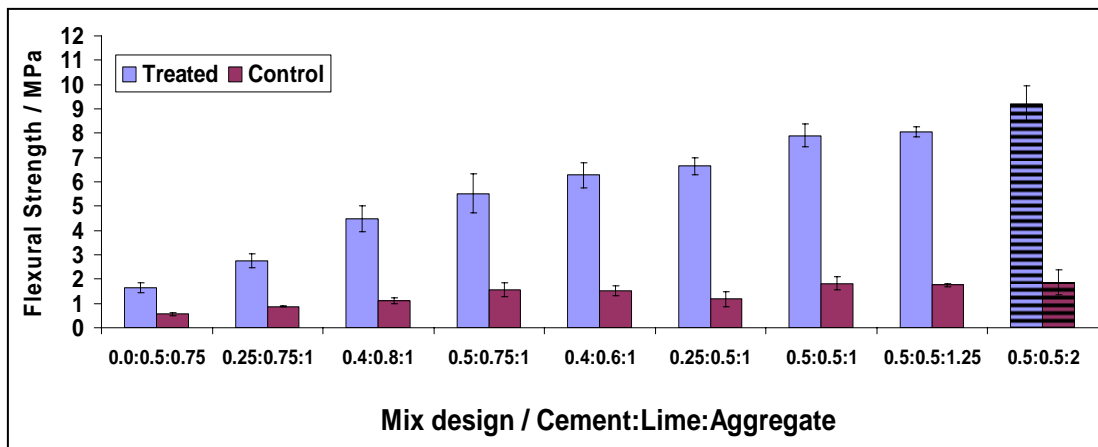
<b>C1</b>	P→preC → scCO <sub>2</sub> →test both control and carbonated
<b>C1-28</b>	P→preC → scCO <sub>2</sub> →C28→test both control and carbonated
<b>C3</b>	P→C3 →preC→ scCO <sub>2</sub> →test both control and carbonated
<b>C3-28</b>	P→ C3 →preC → scCO <sub>2</sub> →C28→test both control and carbonated
<b>C7</b>	P→C7 →preC→ scCO <sub>2</sub> →test both control and carbonated
<b>C7-28</b>	P→ C7 →preC → scCO <sub>2</sub> →C28→test both control and carbonated
<b>C3*</b>	P→ preC→ scCO <sub>2</sub> →C3→test both control and carbonated
<b>C3*-28</b>	P →preC → scCO <sub>2</sub> →C3→ C28→test both control and carbonated
<b>C7*</b>	P→ preC→ scCO <sub>2</sub> →C7→test both control and carbonated
<b>C7*-28</b>	P →preC → scCO <sub>2</sub> →C7→ C28→test both control and carbonated
P: processed green forms via compression moulding PreC= Pre-carbonation conditioning by oven drying at 25°C for 12 hr. C = Conditioned in water for duration of 3, 7,28 , etc day scCO <sub>2</sub> = Supercritical carbonation for 24 hr at 100Bar and 60°C	

Pre-carbonation moisture content or ‘degree of drying’ (DOD, expressed as a percentage of the total weight loss achieved by drying to constant weight at 105°C) of the green specimens were adjusted by oven drying at 25°C for approximately 12 hr, as previous studies have shown that DOD influences the efficacy of supercritical carbonation. This produces a DOD of around 75%. Samples were then treated with water-saturated scCO<sub>2</sub> at 100 bar and 60°C for 24hr using a sealed heated stainless steel vessel (internal dimensions Ø100 × 500 mm) in which a measured quantity of dry ice is allowed to vaporise. Control samples were stored in a sealed jar for the period in which treated samples were carbonated. Some samples were also subjected to further pre- or post-carbonation curing regimes as detailed in table 1.

Degree of carbonation was determined semi-quantitatively by using XRD to measure depletion of calcium hydroxide (CH) and alite (C<sub>3</sub>S). Flexural strength was measured using a fully articulated 4-point bending rig on a 100 kN Testometric test machine. The microstructural investigation of the control and carbonated samples was carried out using TSP and SEM. TSP has been shown to be a very useful method for examining the microstructure of a cementitious composite when authoritative identification of phases is required [6]. To study the effect of scCO<sub>2</sub> and water curing regimes on the microstructure of composites, standard 30µm petrographic thin sections were prepared from the control and carbonated samples exposed to different water curing regimes. The slides were then examined under the modified Vickers petrological microscope, using plane polarised, dark field plane polarised and cross-polarised light.

### 3. Results

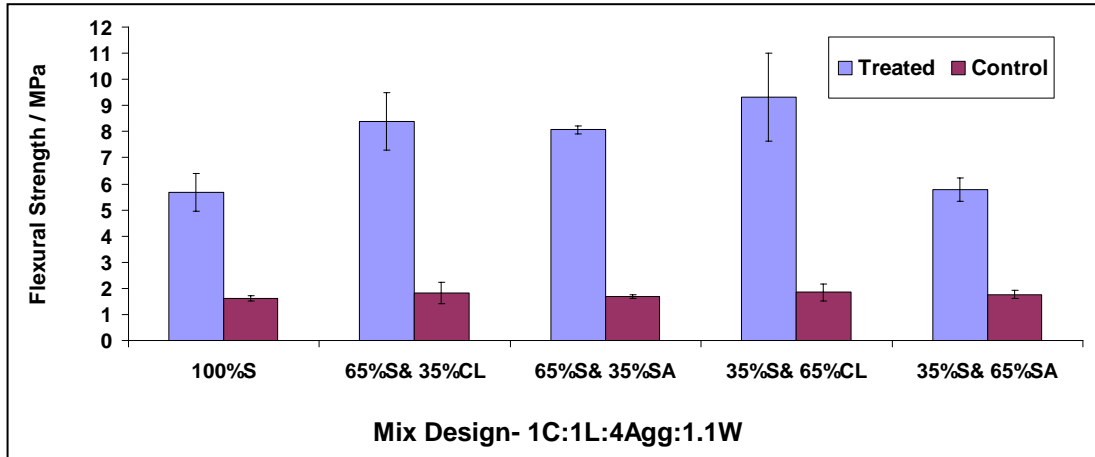
#### 3.1 Mechanical Testing



**Fig. 1: Flexural strength vs. Mix design.** Treated= scCO<sub>2</sub>, 60°C, 100bar,24Hr. Aggregate= 65%S,35% CL. All proportions w:w. Error bars= ±st. dev. Curing regime C1.

Figure 1 shows control and treated strength for various preliminary mix designs. Flexural strength ( $\sigma$ ) increased with C: L ratio and aggregate content. Treated

samples containing cement were much stronger than those without cement. Aggregate composition in these mix designs was a combination 35:65 w/w CL:S.



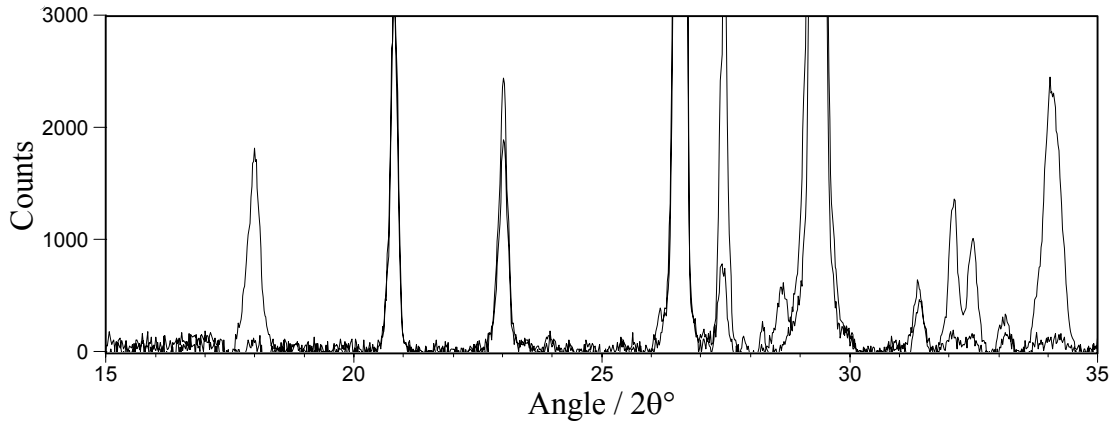
**Fig. 2. Flexural Strength vs. Mix design.** Treated= scCO<sub>2</sub>, 60°C, 100bar, 24Hr. Aggregate content as shown. Error bars= ±st. dev. Curing regime C1.

To investigate the effect of changes in aggregate composition, experiments were carried out using the optimum mix design highlighted in Figure 1 and having 5 different scenarios for the aggregate composition (Figure 2). Engineered silica aggregate (SA) was used in some of the mixes as a substitute to CL in order to study the effect of changes in aggregate composition independently of any particle size effect. Although the strength of control samples were the same throughout these 5 sets, treated samples with limestone aggregate were stronger than those with only silica (i.e. S and/or SA) aggregate. The effect is more marked as the limestone content increases; 65:35 CL:S were significantly stronger than the rest.

Results from mechanical testing on samples exposed to the various curing regimes revealed that for treated samples, no significant benefit was gained from any period of water curing prior to or after carbonation. Control samples gained strength in the expected manner. The flexural strength of treated samples exposed to carbonation immediately after demoulding/preC i.e. the simplest, shortest curing regime (C1, table 1) was up to 60% higher than that achieved by normal 28-day curing of uncarbonated samples; the carbonation process adds strength over and above that expected through curing alone. Carbonation immediately after demoulding/pre-conditioning would be the preferred industrial option since it produces enhanced strength without the need for long-term curing.

### 3.2 Chemical Analysis / XRD

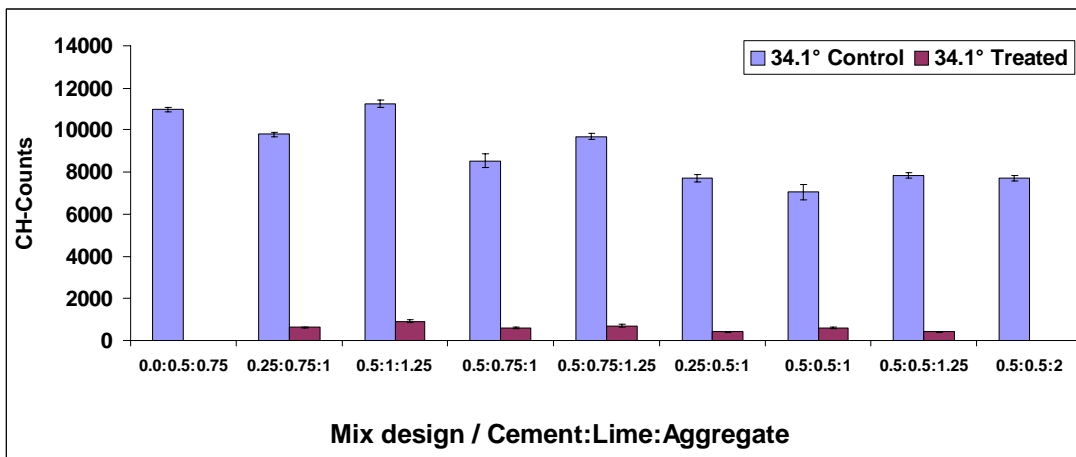
Figure 3 shows a portion of a typical XRD trace for control and carbonated samples (in this case, C1 table 1).



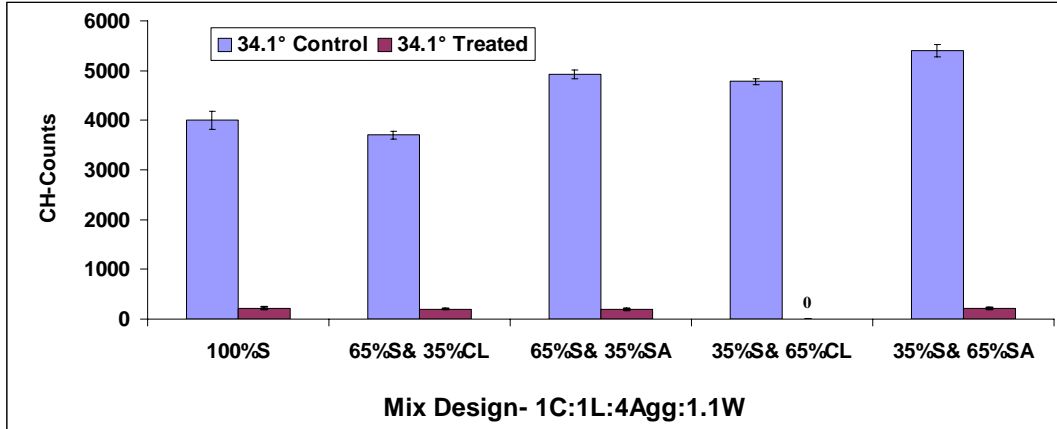
**Fig. 3: Comparison between C1-Control and Treated samples.** Angles refer to  $2\theta$  CuK $\alpha$  peaks. Solid lines = treated, dashed lines = control samples.

The key peaks are those at  $18.1^\circ$  and  $34.1^\circ$  indicative of calcium hydroxide (CH), and the double peak at around  $32^\circ$  indicative of unhydrated  $C_3S$ . Both these compounds are significantly depleted by treatment, with a corresponding rise in the various peaks for calcite (note these cannot be used to track carbonation as carbonate aggregates are used in many samples).

The following figures track the evolution of the peaks of interest to express degree of carbonation. Figures 4 and 5 show the degree of CH depletion caused by the carbonation for the specimens represented in figures 1 and 2 respectively. Depletion was generally  $>90\%$ . In all these samples,  $C_3S$  was depleted by the treatment to below the detection limit suggesting that  $C_3S$  is more susceptible to carbonation than CH.

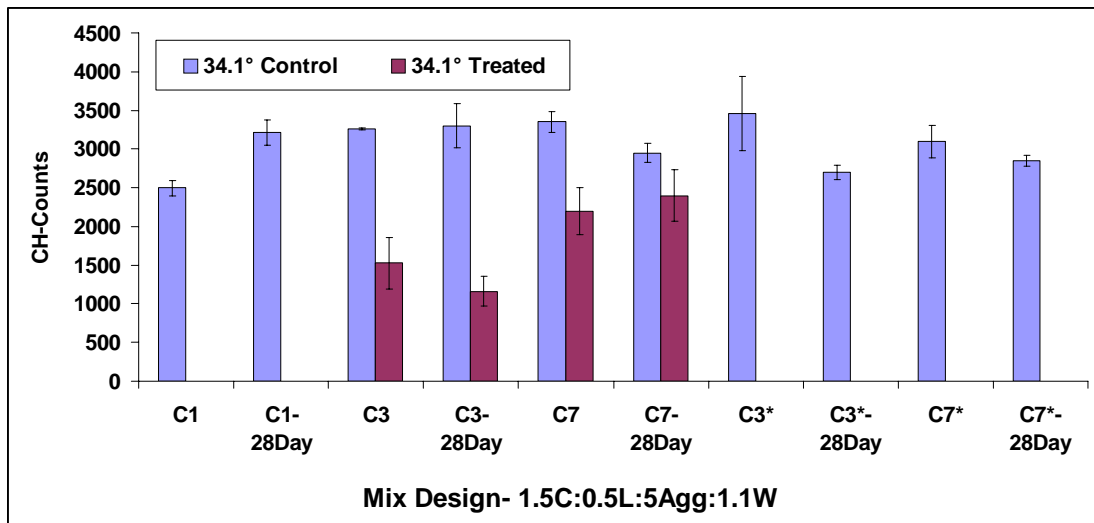


**Fig. 4: XRD analysis of CH depletion vs. mix design.** Samples as Fig. 1. Angles refer to  $2\theta$  CuK $\alpha$  peaks. Average of triplicate Samples. Error bars =  $\pm 1$  st. dev. Curing regime C1.



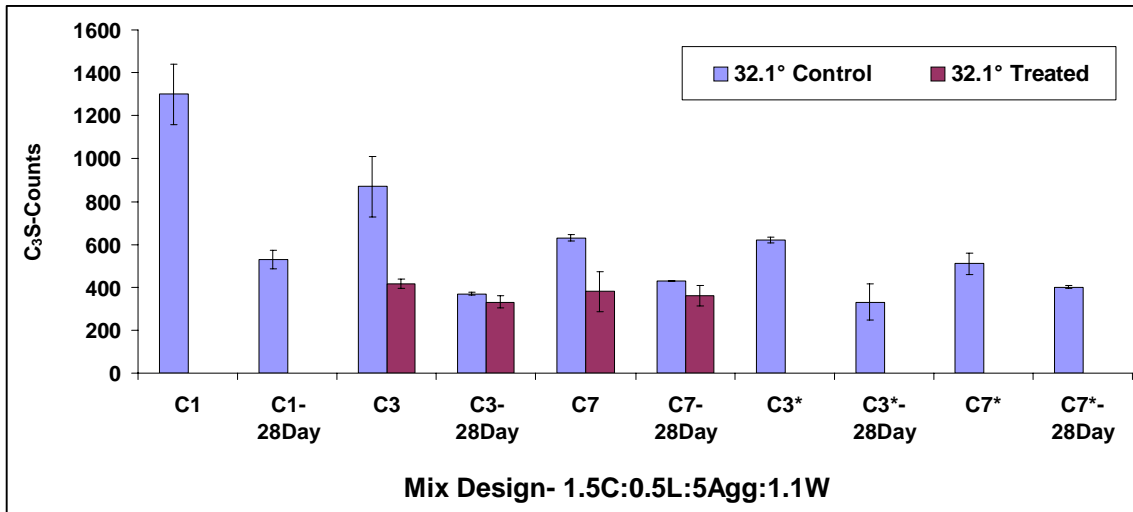
**Fig. 5: XRD analysis of CH depletion vs. mix design.** Samples as Fig. 2. Angles refer to  $2\theta$  CuK $\alpha$  peaks. Average of triplicate samples. Curing regime C1. Error bars =  $\pm 1$  st. dev.

Figures 6 and 7 show the degree to which CH and C<sub>3</sub>S were depleted by the treatment for samples exposed to a wider range of curing regimes (see table 1).



**Fig. 6: XRD analysis of CH depletion vs. curing regime.** Angles refer to  $2\theta$  CuK $\alpha$  peaks. Average of triplicate samples. Error bars =  $\pm 1$  st. dev.

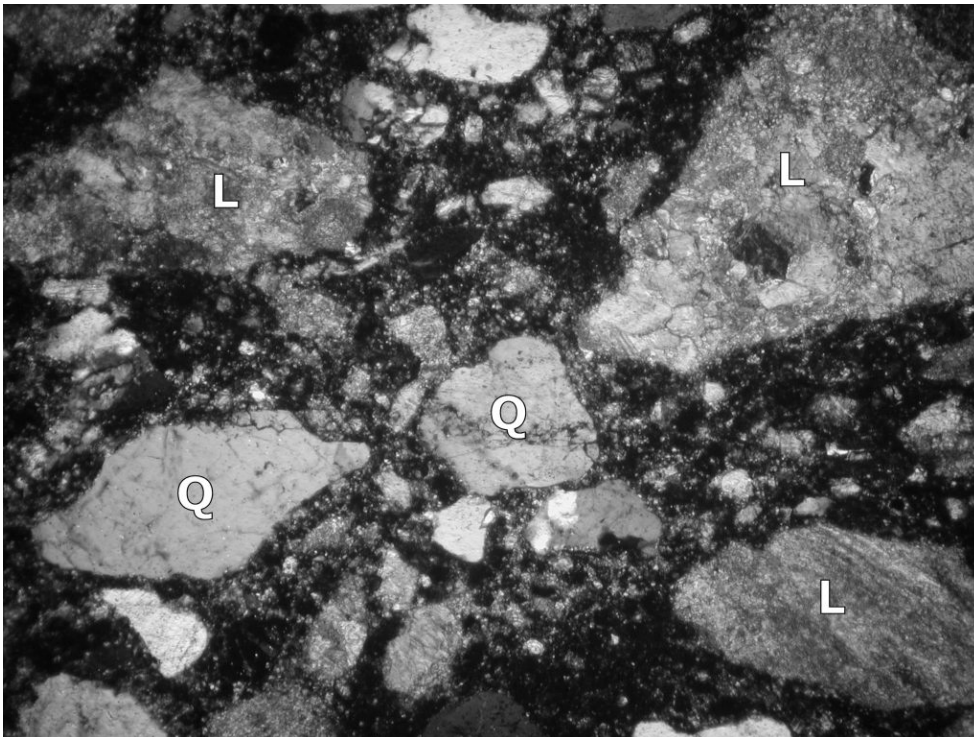
Results indicated complete depletion of CH and C<sub>3</sub>S in treated samples exposed to: immediate carbonation (C1) and no further development of CH during post carbonation curing (C1-28, C3\*, C3\*-28, C7\*, C7\*-28). Treated samples exposed to pre-carbonation curing (C3, C3-28, C7, C7-28) were resistant to carbonation and considerable amounts of CH and C<sub>3</sub>S were detected in the structure after carbonation. The remaining C<sub>3</sub>S appeared to be less able to hydrate in carbonated samples, since the proportion of remaining C<sub>3</sub>S further hydrated during post treatment curing was much smaller for carbonated samples cf. control samples. CH did not reappear in samples cured after treatment, indicating that no amorphous C<sub>3</sub>S (that XRD would not detect) is left after treatment for secondary hydration.



**Fig. 7: XRD analysis of C<sub>3</sub>S depletion vs. curing regime.** Angles refer to 2θ CuKα peaks. Average of triplicate samples. Error bars = ± 1 st. dev.

### 3.3 Microstructural analysis

Figure 8 shows the microstructure of a control (C1) sample. Typical limestone (L) and sand (i.e. quartz, Q) particles have been marked.



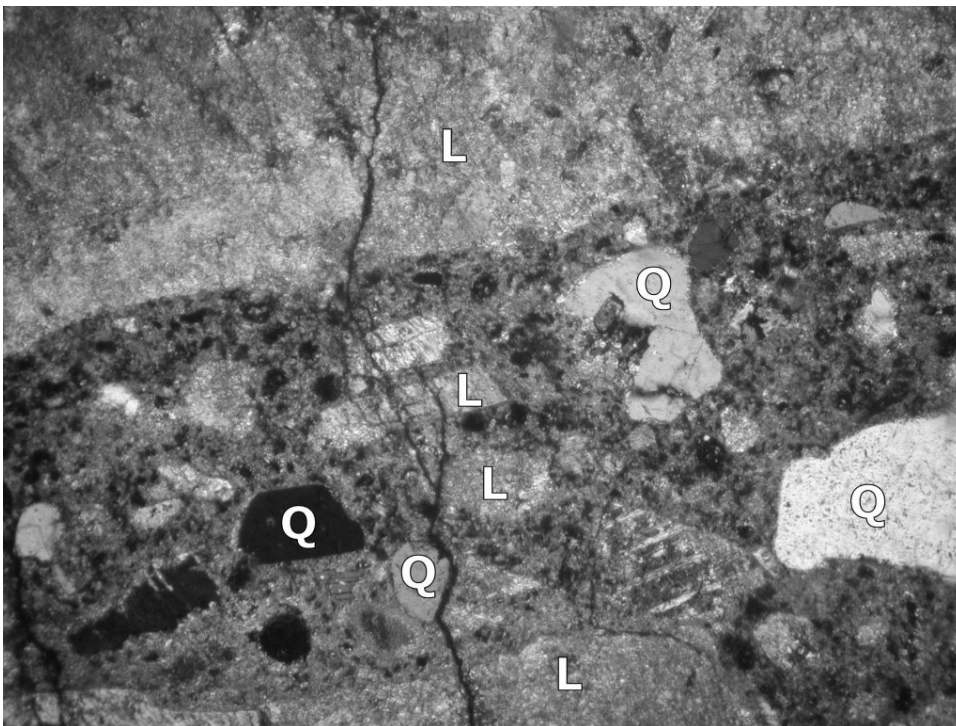
**Fig. 8. Thin section micrograph of C1 control sample.** Crossed polars, horizontal field of view = 1.4mm.

The groundmass – the material between the aggregate particles – is generally dark, owing to the poorly crystalline unhydrated cement minerals and some CSH gel, studded with bright flecks of small calcium hydroxide crystals. The interface

between the aggregate particles and the groundmass is not intimate and some porosity can be observed.

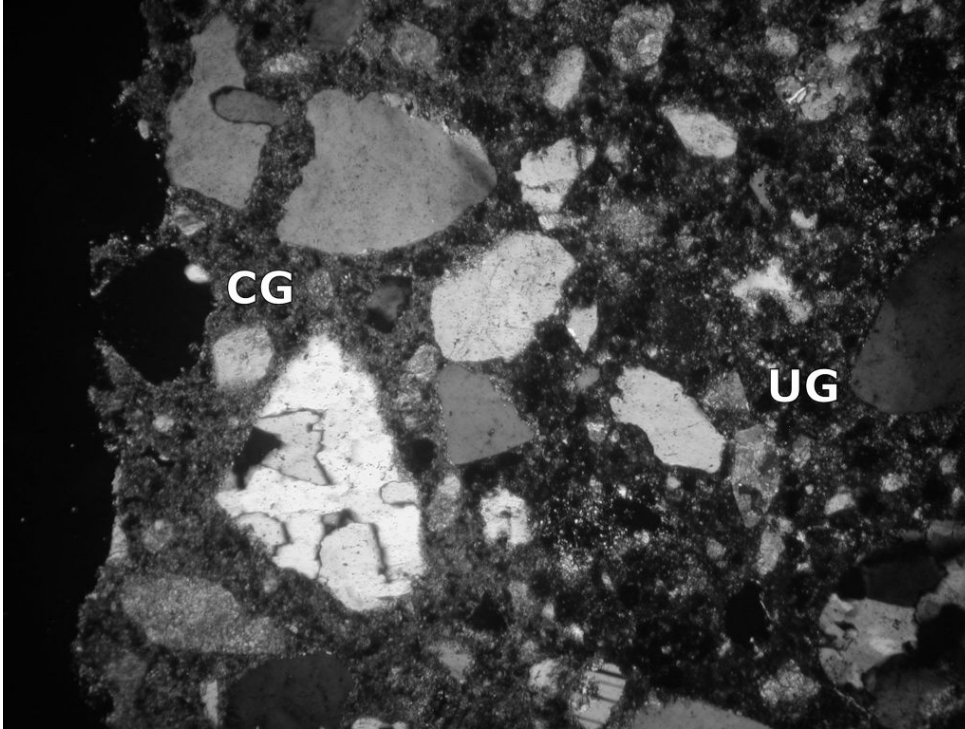
Figure 9 shows a carbonated (C1) sample. The groundmass is much lighter, composed of cryptocrystalline calcium carbonate (identifiable by its high birefringence) mixed with an amorphous phase, presumably decalcified CSH gel. The dark inclusions are pseudomorphs of unhydrated cement grains which have been carbonated. There is very little porosity at the interface, it seemingly having been filled with cryptocrystalline calcium carbonate; indeed, the interface between the limestone and the groundmass is now quite indistinct in places. A crack (caused by mechanical testing, not the carbonation process) can be seen passing through the limestone aggregate particles but around the quartz particles. This indicates that the matrix has attained a strength comparable to that of the limestone aggregate and the bond between the two is very good, while the quartz aggregate is rather stronger and may not be as well bonded.

Figure 10 shows a sample that has been cured prior to carbonation (C7-28). The sample surface, as exposed to  $scCO_2$  can be seen on the left of the figure. The penetration of the  $scCO_2$  has been impeded by the cured microstructure; only a relatively shallow layer near the surface has fully carbonated groundmass (CG), while deeper in the sample it remains largely uncarbonated (UG).



**Fig. 9. Thin section micrograph of C1  $scCO_2$  treated sample.** Crossed polars, horizontal field of view = 1.4mm.





**Fig. 10. Thin section micrograph of C7-28 scCO<sub>2</sub> treated sample. Crossed polars, horizontal field of view = 1.4mm.**

#### **4. Discussion**

Full carbonation (as measured by CH and/or C<sub>3</sub>S depletion) is not necessarily an indicator of good strength development in treated samples; the mix design plays a critically important role in strength of treated specimens. Comparing Figures 4 and 1, and also 5 and 2, it can be seen that there is little if any correlation between degree of carbonation and treated strength. Samples cured underwater prior to treatment are resistant to carbonation. The more developed cured microstructure, with lower porosity and permeability, resists the ingress of scCO<sub>2</sub>. However, this does not seem to affect the treated strength, which remains around twice that of untreated samples similarly cured. This suggests that even in samples in which a significant proportion of the calcium hydroxide and/or C<sub>3</sub>S has not carbonated, the strength bearing phase – i.e. the CSH – has been significantly affected by the scCO<sub>2</sub> treatment.

Treated samples containing cement were much stronger than those without (i.e. lime only), despite being fully carbonated by the treatment, suggesting that the binding ability of the carbonated CSH gel is far greater than that of interlocking calcium carbonate crystals although more research is required.

The results in Figure 2 show that using limestone aggregate has an effect on treated strength over and above any effect that can be attributed to particle size distribution (e.g. packing). Since the limestone is weaker than the siliceous aggregates (as evidenced in Fig. 9), the effect is most likely caused by increased

bond between CL and the matrix compared with that of SA/S. The strength of the control samples with any aggregate are similar; the effect is particular to carbonated samples, thus differences in surface texture or shape cannot explain the phenomenon. It seems likely therefore that the surface of the carbonate aggregate preferentially encourages nucleation of calcium carbonate at the CL: matrix interface during carbonation, compared with the SA/S: matrix interface, encouraging good bond. The observation of an indistinct, intimate interface between CL particles and carbonated matrices would support this thesis.

## 5. Conclusions

1. Over the range studied, all samples were more or less fully depleted with regard to CH and  $C_3S$  content after carbonation as indicated by XRD. The exception to this was samples cured in water prior to carbonation, in which some CH and  $C_3S$  remained. 'Wet' (i.e. not pre-conditioned) samples were resistant to carbonation.
2.  $C_3S$  depletion, over the entire range of samples studied, was more marked than CH depletion during carbonation. Thus  $C_3S$  would appear to be more susceptible to carbonation than CH.
3. Carbonated samples made with a higher proportion of limestone aggregates were significantly stronger than those made with higher proportion of silica aggregates, independent of particle size distribution effects or degree of depletion of CH. Thus the limestone is likely to have some physico-chemical effect on the carbonation process and subsequent development of carbonated microstructure.
4. Compared with the flexural strength achieved by carbonating samples after immediately after demoulding/ pre-carbonation conditioning, no significant benefit was gained from any period of water curing either prior or post –carbonation. The flexural strength of treated uncured samples (C1) was about 60% higher than that achieved by normal 28-day curing of uncarbonated samples. Thus carbonating immediately after demoulding/pre-conditioning is the preferred industrial option.

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