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Preliminary investigations of the phase composition and fine pore structure of super-critically carbonated cement pastes

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Super-critical carbonation of cement-based materials can lead to significant improvements in their properties. Preliminary investigations suggested that processing should be aimed at producing a matrix material with minimal amounts of $Ca(OH)_2$, anhydrous material and C—S—H gel along with a controlled pore structure. Using ^{29}Si MAS NMR and TGA as the principal investigative techniques it has been shown that moisture content during carbonation is a major factor in determining the phase composition and pore structure of the resulting matrix. Of the drying regimes studied, 60% DOD gave the greatest amount of conversion to calcium carbonate and silica gel.

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1. Introduction

The advantages of treating hardened cement paste with super-critical carbon dioxide ($scCO_2$), where chemical reactions occur between the $scCO_2$ and the cement hydrates to produce a carbonated material, were originally described by Jones *et al.* [1]. Investigations in our laboratories have shown that the properties of glass fibre reinforced cement (grc) may be substantially improved by super-critical carbonation [2, 3] so that: (a) for unaged, carbonated grc there were significant increases in matrix strength, design toughness and frictional bond strength; (b) carbonated samples retained significant toughness after ageing while control samples were completely degraded; and (c) carbonated samples exposed to a number of different environments were much more dimensionally stable than uncarbonated specimens.

Progress has been made in relating these enhanced properties to some of the process variables employed and subsequent changes in microstucture [4]. Thus the improvements in long-term durability were associated with reduction in the pH of the pore solution, and substantial conversion of calcium hydroxide, anhydrous material and C—S—H gel to calcium carbonate and silica gel. Improved mechanical properties and dimensional stability were attributed to substantial reductions in total porosity and modifications in micro-pore structure respectively.

Results suggest that, for optimum properties, processing should be aimed at producing a matrix material with minimal amounts of calcium hydroxide, anhydrous material and C—S—H gel along with a controlled pore structure. To facilitate this a better understanding of the carbonation reactions is needed. The aim of the studies reported in this paper was to improve our understanding of the nature of the carbonation reactions and their influence on pore structure. In particular, the conversion of C—S—H gel and anhydrous material to calcium carbonate and silica gel was studied using NMR and TGA as the investigative techniques.

2. Experimental

2.1. Materials and specimen preparation

In previous investigations [2–4] a normal Portland cement was used. However, these studies were carried out using a white Portland cement to facilitate the NMR examinations. Its composition expressed in percentages by weight of the constituent oxides and phases present, is given in Table I. Pastes were made using de-ionised

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TABLE I Oxide and compound composition of the white Portland cement

Oxide	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	Alkalis	MgO	Free lime	Cl	LOI[a]
% w/w	68.90	24.81	1.93	0.32	1.74	0.28	0.73	2.2	0	0.62
Phase potential		C_3S	C_2S	C_3A	C_4AF					
% w/w		64.5	22.6	4.6	1.0					

[a] LOI: loss on ignition.

water at a water/cement ratio (w/c) of 0.6 and cast into 48 × 75 mm cylindrical moulds. They were then vibrated for 1 min to remove air bubbles and sealed. After curing at 20°C for 24 h, the cylinders were de-moulded and cut into 10 mm thick slices.

Earlier investigations [2–4] showed that the nature of the carbonation reactions, and ultimately the properties achieved, depended on the amount of water present in the specimens prior to treatment. This moisture content was expressed as the degree of drying (DOD) where DOD = mass loss after equilibrating at a given RH/mass loss after oven drying at 105°C. In the present investigations, the slices were conditioned by storing in sealed boxes at 20°C and either 95 or 35% RH, or in an oven at 105°C for 7 days, to give DODs of approximately 0, 60 and 100% respectively [2]. Whilst the optimum DOD has not been firmly established, property measurements made so far suggest that it is around 60%.

Specimens were then statically exposed to $scCO_2$ at 59°C and 97 bar for 24 h [2]. On removal from the vessel they were immersed in propan-2-ol to remove any free water present and prevent further hydration. Control samples were conditioned in the same manner but immersed straight into propan-2-ol rather than carbonated. Prior to analysis the propan-2-ol was removed by evacuation or warming at ~50°C.

2.2. Analytical techniques

For combined differential thermal analysis/thermogravimetry (DTA/TGA), specimens were ground to pass a 150 μm sieve and analysed in air between 20 and 1000°C at a heating rate of 20°C min^{-1}. Features were checked using duplicate samples. The TG data obtained for the carbonated samples were corrected for the mass gain through uptake of CO_2.

NMR spectra were acquired using a Bruker MSL300 spectrometer equipped with an Oxford Instruments 7.1T super-conducting magnet. Spectra for ^{29}Si were acquired at 59.6 MHz with magic angle spinning (MAS) at 3.5 kHz using 7 mm zirconia rotors and ^1H decoupling at approximately 40 kHz. Chemical shifts were referenced to tetramethylsilane, using tetrakis(trimethylsilyl)siloxane (−9.9 ppm) [5] as a secondary reference. Spectra of control (uncarbonated) samples were quantified by simple integration; whilst for the more complex spectra of carbonated specimens, curve-fitting procedures were required. Igor Pro software [Wavemetrics, Oregon, USA] was used, with additional macros by Brough.

Pore size distribution studies were carried out by mercury intrusion porosimetry (MIP), the results being analysed by means of the Washburn equation with assumed values of 117° for the contact angle and 0.485 Nm^{-1} for the surface tension of mercury.

3. Results and discussion

3.1. TG and NMR analyses

3.1.1. Control specimens

The three preconditioning regimes used will have influenced the degree of hydration of the specimens prior to carbonation. Thus samples conditioned at 0% DOD will have continued to hydrate for 7 days, whilst for samples at 100% DOD, hydration will have effectively ceased after 1 day. At 60% DOD hydration will have continued for a little longer than 1 day as the samples came to equilibrium. These differences in degree of hydration are reflected in the data obtained from the TGA (Table II) and NMR (Table III) analyses. In the quantification of the NMR spectra, shown in Fig. 1, it should be noted that numbers relate to the proportions of the silicate groups in the different phases, not to mass percentages of phases.

For a DOD of 0% the degree of hydration was 73%, which is similar to that obtained for a C_3S paste with similar w/c which gave a figure of around 70% at 7 days [6]. As the DOD increased the amounts of anhydrous material remaining also increased showing significantly less hydration in these specimens. The quantities of $Ca(OH)_2$ as shown by TGA, correlate reasonably well with the degree of silicate hydration measured by NMR, indicating no major changes in the mode of hydration as a result of the preconditioning treatment.

TABLE II Quantitative analysis of the TG data (%w/w)

DOD (%)	Control $Ca(OH)_2$	Carbonated $Ca(OH)_2$	$CaCO_3$	[a]
0	13.6	trace	30.6	12
60	9.7	2.9	32.4	23
100	7.4	6.5	18.6	17

[a] $CaCO_3$ content of treated sample not accounted for by conversion of $Ca(OH)_2$, as measured in the control specimens.

TABLE III Relative proportions of ^{29}Si contained in anhydrous material, C—S—H gel and silica gel from NMR

	Control		Carbonated		
DOD (%)	Anhydrous material	C—S—H gel	Anhydrous material	C—S—H gel	Silica gel
0	27	73	5	36	59
60	60	40	2	10	89
100	68	32	15	3	83

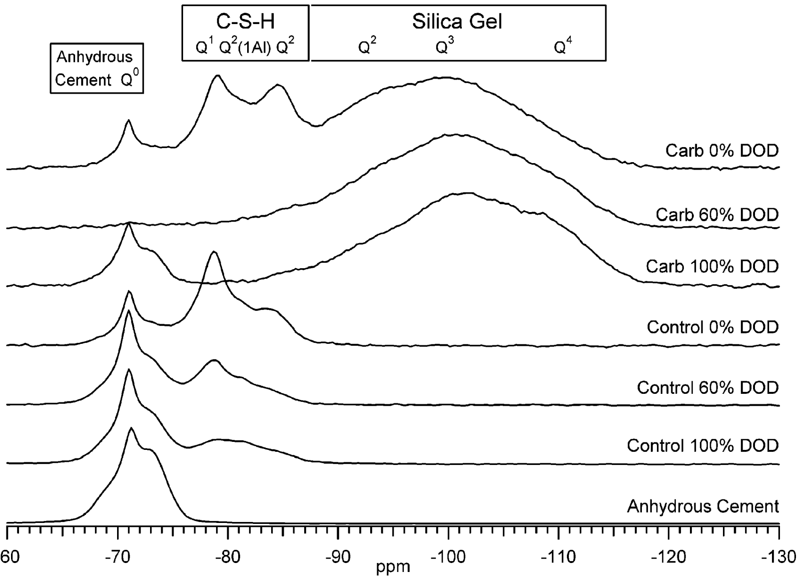

Figure 1 NMR Spectra with associated curve fitting.

The amount of C—S—H gel produced decreased as the DOD increased, but in all three cases was structurally similar to gel observed previously [6], containing short chains (predominantly end chain Q^1 groups at -79 ppm with minimal Q^2 and Q^2(1Al) middle chain species at -82.5 and -85 ppm respectively) although a quantitative analysis of chain length was not performed. Visual observation of the spectra, Fig. 1, confirms that alite (the broad peak from -67 to -76 ppm) reacted faster than belite (sharper superimposed peak at -71 ppm) as expected.

3.1.2. Carbonated specimens

The amounts of $Ca(OH)_2$ and $CaCO_3$ as determined by TGA are given in Table II and the relative amounts of anhydrous material, C—S—H gel and silica gel as determined by NMR are given in Table III. The amounts of calcium carbonate produced, but not accounted for by conversion of $Ca(OH)_2$ (Table II), are reasonably (but not entirely) consistent with the amounts of silica gel produced (Table III). Fig. 2 shows the NMR spectra with associated curve fitting. The fits for the anhydrous cement remaining do not attempt to reproduce the complex cement peak shape, but should give good estimates of the area of this peak.

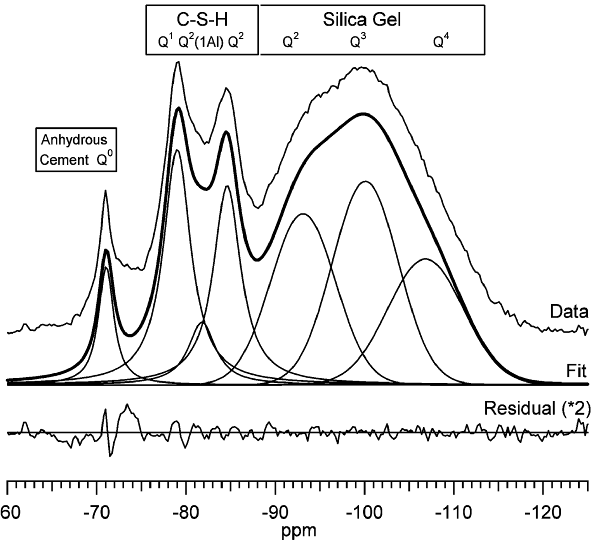

Figure 2 MIP pore size distribution curves.

In all of the carbonated specimens, the amounts of reaction are substantially increased relative to the controls with much lower quantities of anhydrous material remaining in the samples. However it is not possible to say what proportion of this increase is due to carbonation and what proportion is due to the raised temperature and further curing during the carbonation process. An estimate can be made assuming reaction rates roughly double for every 10°C increase in temperature, then 1 day at 59°C would correspond to about 2 weeks at 20°C. Thus reaction would be expected to increase to approximately 80% for the non-dried specimen for which experimentally, 15% of anhydrous material remains. In practice at higher temperatures, hydration tends to be retarded at later ages by growth of dense reaction rims. Therefore it appears that the carbonation process does lead to some additional reaction of the anhydrous material.

The nature of the carbonated gel cannot directly be determined from the NMR spectra. In addition to some fully cross-linked Q^4 species, the predominant ones are Q^3 cross-linked species with additionally, some Q^2 chain species. In Q^3 and Q^2 species, 1, or 2 respectively of the Si—O—Si linkages are replaced by Si—OH or Si—O(Ca)$_{0.5}$ species. These two possibilities have closely similar chemical shifts, and cannot be distinguished based on shifts. However if the samples are fired to 400°C then Si—OH groups can be eliminated by dehydration [7], which is not the case for SiOCa linkages. However when this was carried out, substantial changes in structure took place and the experiment was inconclusive. Samples carbonated at 0% DOD showed an increased proportion of Q^2 and a reduced amount of Q^4 as compared to samples carbonated at 60 and 100% DOD, Table IV. This indicated an opening up of the gel in the wetter specimens and can be summarised by the

TABLE IV Relative proportions and chemical shifts of Q^2, Q^3 and Q^4 in the silica gel of carbonated samples

DOD (%)	% Q^2	Shift Q^2 (ppm)	% Q^3	Shift Q^3 (ppm)	% Q^4	Shift Q^4 (ppm)	Mean Q No.
0	33	−93.1	39	−100.1	28	−106.8	2.95
60	23	−93.1	47	−100.6	30	−108.4	3.06
100	22	−93.0	43	−100.9	35	−108.9	3.13

TABLE V Nature of porosity from MIP

	Control			Carbonated		
DOD (%)	0	60	100	0	60	100
Initial pore entry diameter (μm)	0.60	0.90	0.90	0.09	0.30	0.90
Large pores > 30 nm (cc g^{-1})	0.09	0.23	0.30	0.04	0.06	0.15
Small pores < 30 nm (cc g^{-1})	0.11	0.04	0.06	0.09	0.07	0.02
Total intrusion volume (cc g^{-1})	0.20	0.27	0.36	0.13	0.13	0.17

gradual increase of mean Q number from 2.95 in the wetter samples to 3.13 in the drier samples.

An additional factor determining chemical shifts is the Si—O—Si bond angles, with open flexible gels having lower bond angle and shifts that are numerically higher [8], e.g., Q^4 at −107 ppm in an open gel. More closely packed structures have larger bond angles and numerically lower shifts for example, silica fume at −110 ppm. In the carbonated materials discussed in this paper, the Q^4 peaks gradually shift on going from dry to wet carbonated conditions, from −109 to −107 ppm probably caused by the opening of the silica gel. Similar shift changes, although somewhat smaller are observed for the Q^3 species, again consistent with an opening of the gel.

The silica gel may also be slightly substituted. This would lead to Q^4(1Al) and Q^3(1Al) peaks at approximately −105 and −95 ppm respectively. Such peaks are not observed as distinct shoulders, indicating that such species are not predominant. However, small quantities of these species may be present, obscured by the overlaps between the main Q^n(0Al) peaks. We have not attempted to fit such substituted species since the data is insufficiently resolved to make such fits useful.

Why the preconditioning treatment should have this effect is not clear at the moment but it may be related to whether the silica gel is produced by carbonation of C—S—H gel or a process whereby anhydrous material is converted directly to carbonate and silica gel without intermediate formation of C—S—H gel. Examination of the data in Table III shows that for samples conditioned at 0% DOD, of the silica gel produced approximately 2/3 is from carbonation of the C—S—H gel and 1/3 from direct carbonation of anhydrous material. In contrast for samples conditioned at 60 and 100% DOD, of the silica gel produced approximately 1/3 is from carbonation of C—S—H gel and 2/3 from carbonation of anhydrous material.

3.2. Mercury porosimetry

The MIP pore size distribution curves are shown in Fig. 3 with key data obtained from them compiled in Table V. The influence of the three preconditioning regimes on the pore size distribution found prior to carbonation is quite apparent. Thus for DODs of 0, 60, 100%, the initial pore entry diameters are 0.60, 0.90, 0.90 μm and total intrusion volumes are 0.20, 0.27, 0.36 cc g^{-1} respectively. Thus as DOD increases there is a shift to coarser pore structures and large porosities as might be expected. After supercritical carbonation the initial pore entry diameters for DODs of 0 and 60% have been reduced to 0.09 and 0.30 μm respectively whilst for a DOD of 100% it stays the same. Total porosities are reduced to 0.13, 0.13, 0.17 cc g^{-1} respectively.

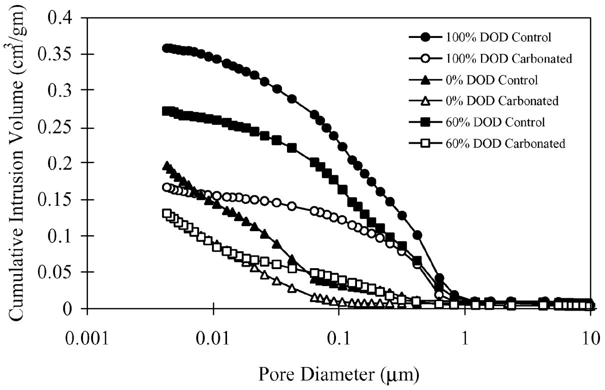

Figure 3 General NMR spectra of control and carbonated cements.

It should be noted that for a given DOD the volume of sub 30 nm pores in the control samples, 0.11, 0.04, 0.06 cc g^{-1}, correlates well with the amount of C—S—H gel present, 73, 40, 32% respectively. After carbonation the volumes of this porosity are very similar although now it must be in the silica gel.

3.3. General comments

It is evident from the results in Tables II and III that the preconditioning treatment is very important in determining the phase composition after carbonation and in turn the influence this has on pore structure, Fig. 3. Thus for a 100% DOD, virtually all the C—S—H gel and most of the anhydrous material has been carbonated, although most of the calcium hydroxide remains. Whilst total porosity is considerably reduced a significant fraction of that remaining is coarse porosity with no change in initial pore entry diameter. Such changes lead to improvement in unaged mechanical properties of grc but not long-term durability [2].

For a 0% DOD virtually all the anhydrous material is carbonated. There is only a trace of calcium hydroxide but a substantial amount of C—S—H gel remains. This resulted in the most favourable pore structure, but grc material still had reduced long-term durability [2], presumably influenced in some way by release of alkali that had been adsorbed in the C—S—H gel. For a 60% DOD virtually all anhydrous material is carbonated whilst small amounts of C—S—H gel and CH remain leaving a slightly coarser pore structure than that found at 0%

DOD. This phase composition and pore structure does however show the best overall properties for grc.

It would also appear from the results in Table III that it is easier to carbonate anhydrous material than gel—there may even be a limit to the amount of gel that can be carbonated. This suggests reducing hydration times prior to carbonation would be beneficial.

It is evident that competing factors are at work and complete optimisation of the carbonation parameters has not been reached. In addition other factors such as w/c need to be investigated. This approach is probably sound since most of the matrix has been converted to calcium carbonate and a (calcium modified) silica gel.

Substantially improved dimensional stability of grc specimens after super-critical carbonation was attributed to modifications in micro-pore structure of the mortar matrix [3]. Specimens for that work had been conditioned at 60% DOD. Reference to Table V shows that sub 30 nm porosity actually increased after carbonation from 0.04 to 0.07 cc g^{-1} which suggests that dimensional stability should have been worse. That it is not may be attributed to conversion of C—S—H gel to silica gel where the pores have a different geometry (highly cross-linked silica gel compared to C—S—H slits). This seems a very interesting observation given the relatively open nature of the silica gel at the ångstrom level. In contrast ASR gels are dimensionally unstable, although they probably contain a lot less Q^4 and more Q^2.

4. Conclusions

These investigations have confirmed that the initial moisture content of the cement paste governs the amount of calcium hydroxide, anhydrous material and C—S—H gel remaining after carbonation. In turn the relative amounts of phases converted influence the pore structure. A 60% DOD gives the greatest amount of conversion to calcium carbonate and silica gel. Combining techniques such as NMR, TGA and MIP is a very useful approach in establishing the nature and porosity of carbonated phases, and their relationship to engineering properties such as flexural strength, toughness and dimensional stability.

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