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Preliminary investigations into the supercritical carbonation of cement pastes

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Interactions between supercritical carbon dioxide ($scCO_2$) and hydrated cement pastes, of various water/cement ratio, have been investigated. The carbonation process was greatly accelerated in the $scCO_2$ compared to that in natural or CO_2 enriched environments. The nature of the reactions was dependent on the amount of water present in the paste. Thus carbonation of samples dried prior to treatment resulted in the reaction of all the unhydrated C_3S and C_2S, but little conversion of calcium hydroxide to calcium carbonate. In contrast, carbonation of samples containing moisture resulted in the conversion of most of the calcium hydroxide whilst the amounts of C_3S and C_2S reacted increased as the water/cement ratio increased. During the carbonation treatment, the pore structure of the cement pastes was altered and substantial reductions in porosity were achieved. The process may be used to improve the durability of glass fibre reinforced cement by lowering the alkalinity and calcium hydroxide content of the matrix.
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1. Introduction

Expansion in the use of glass fibre reinforced cement (grc) has not been achieved because of concern about its long term durability, particularly in wet environments. Chemical degradation of the fibres by hydroxyl ions in the hydrating cement matrix and precipitation of calcium hydroxide crystals within the fibre strands are considered to be the main factors governing the reduction of mechanical properties [1]. In theory, carbonation of grc samples soon after fabrication should mitigate both of these factors and produce a more durable material. In addition, it has been shown that grc samples carbonated for 4 months in CO_2 enriched air at 65%RH had a substantially greater matrix strength and increased toughness when compared to samples cured under water [2]. Similar results combined with increased durability have been found for samples treated using supercritical carbon dioxide ($scCO_2$) as the carbonating atmosphere [3]. In addition, it was possible to reduce the treatment time for carbonation to less than 24 hr for boards ~8 mm thickness.

Supercritical fluids are becoming increasingly important as solvents for use in novel materials synthesis [4]. The advantages of treating hardened cement paste with $scCO_2$, where chemical reactions occur between the $scCO_2$ and the cement hydrates to produce a carbonated material, have been demonstrated [3, 5, 6]. As well as giving improvements in the properties of cement pastes, the process is claimed to have significant environmental benefits, arising from utilisation of CO_2 emissions from e.g. cement kilns [5, 6].

Although improvements in properties have been documented [5, 6], only a little is known about the nature of the chemical reactions occurring during exposure of hardened cements to $scCO_2$ or the parameters controlling them [7]. The main aim of the investigations reported in this paper was to study the reactions occurring between cement and $scCO_2$ particularly in relation to grc production.

2. Experimental

2.1. Materials and specimen preparation

Most of the investigations were carried out with a commercial Portland cement (OPC) of composition, expressed in percentages by weight of the constituent oxides, as given in Table I. Pastes were made using de-ionised water at water/cement ratios (w/c) of 0.4, 0.5, 0.6 and cast into 48 × 75 mm cylindrical moulds. They were then vibrated for 1 minute to remove air bubbles and sealed. After curing at 20°C for 7 days, the cylinders were demoulded and cut into 10 mm thick slices.

A limited number of experiments was carried out using a synthetically prepared mixture of 2 : 1 w/w monoclinic $C_3S : \beta\text{-}C_2S$ to allow study of the reactions of the major cementitious minerals without interference from minor phases such as C_3A. These 'synthetic' pastes were made using de-ionised water at w/c 0.6 and cast into 10 × 50 mm tubes, sealed and cured at 20°C for 7 days.

TABLE I Oxide and compound composition of the OPC

Oxide	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	Alkalis	MgO	Free Lime	Cl	LOI[a]
%w/w	62.8	19.1	4.91	2.87	3.19	0.85	1.50	1.19	0.014	2.34
Phase potential	C_3S	C_2S	C_3A	C_4AF	$C\check{S}$					
%w/w	59	9.9	8.1	8.7	5.4					

[a] LOI: loss on ignition.

Prior to exposure in the $scCO_2$, samples were conditioned for 48 hours in either (a) an oven at 105°C, to remove all the evaporable water or (b) a sealed box at 20°C, 95% RH. Samples were thus classified as 'dry' or 'wet' prior to carbonation.

2.2. Supercritical carbonation

Samples were statically exposed, in a 5.5 litre stainless steel pressure vessel, to either dry or wet $scCO_2$, at 59°C and 97 bar for 24 hours. In the latter case excess water was present so that according to the data of Wiebe and Gaddy [8], the $scCO_2$ was saturated throughout the experiment. The $scCO_2$ was obtained by allowing 1.5 kg of dry ice to decompose in the sealed vessel. Equilibrium was reached after about 25 minutes. Preliminary experiments suggested that this treatment was normally sufficient to cause the samples to carbonate completely (as shown by the phenolphthalein indicator test). After removal from the vessel and to prevent further hydration, free water present in the samples was removed by storing in iso-propanol, followed by evacuation or warming at ~50°C immediately prior to analysis.

2.3. Analytical techniques

For combined differential thermal analysis/thermogravimetry (DTA/TG), 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 DTA thermograms were used only for qualitative purposes, and for ease of comparison here normalised to the calcium hydroxide content. The TG data obtained for the carbonated samples were corrected for the mass gain through uptake of CO_2. Samples for X-ray diffraction (XRD) were similarly ground and the analysis performed using Cu K_α radiation ($\lambda = 0.15418$ nm) between 6 and 60° 2θ at 1° min^{-1}. Angular resolution was 0.1° 2θ. A semi-quantitative assessment of concentrations is given by the relative peak heights. 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

Preliminary experiments indicated that dry $scCO_2$ will not react significantly with dry hardened cement paste, indicating that water must be present either in the sample or in the CO_2 for carbonation to occur.

3.1. Dry samples

3.1.1. Differential thermal/thermogravimetric analyses.

Typical DTA thermograms for samples of w/c 0.4, 0.5, 0.6 which were dried at 105°C (control) and then carbonated are shown in Fig. 1. The presence of $CaCO_3$ formed during treatment is shown clearly by the large endotherm at 700–900°C [9]. A small amount of $CaCO_3$ is present in all the control samples, probably from atmospheric carbonation during sample preparation and/or dissolved CO_2 in the mix water. The temperature at which CO_2 begins to be expelled from the control samples is indistinct, but is probably around 700°C and de-carbonation ceases at around 825°C. In the treated samples, the de-carbonation appears much more clearly defined and occurs at rather higher temperatures, 775–895°C.

The endotherms at 500–550°C are a result of the de-hydroxylation of $Ca(OH)_2$ [10]. It may be noted that the starting temperature of the $Ca(OH)_2$ endotherm in carbonated samples was consistently higher than that in untreated samples. It is suggested that this may be due to only finely divided or crypto-crystalline $Ca(OH)_2$ being carbonated during treatment. The remaining well-crystallised $Ca(OH)_2$ would be expected to start undergoing de-hydroxylation at a higher temperature. In

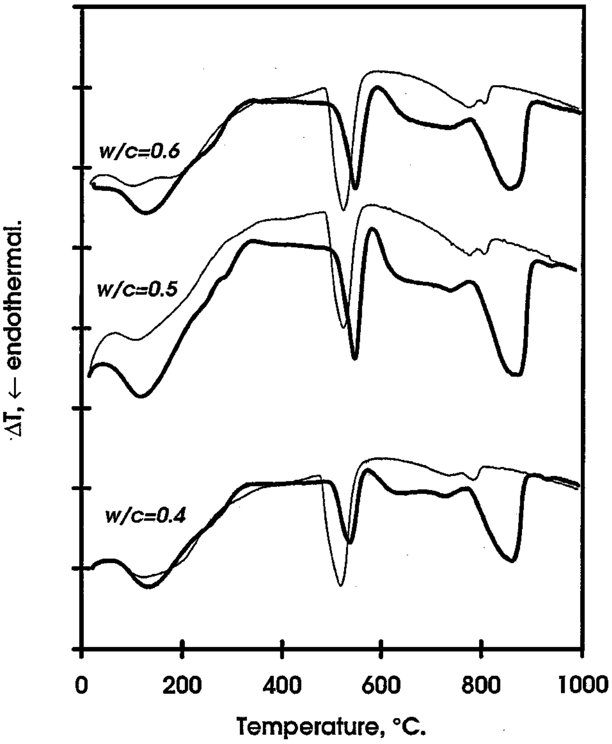

Figure 1 DTA thermograms, dry OPC samples. Fine line: control samples, bold line: carbonated samples.

TABLE II Quantitative analysis of TG traces for the OPC pastes

		A	B	C	D	E	F	G
		Control samples			Treated samples			
	w/c	TG % LTH	%w/w $Ca(OH)_2$	%w/w $CaCO_3$	TG% LTH	%w/w $Ca(OH)_2$	%w/w $CaCO_3$	%w/w
Dry	0.4	4.1	12.7	5.0	3.4	8.2	29.7	18.6
	0.5	5.1	13.2	6.5	4.4	10.4	30.2	20.1
	0.6	4.1	13.6	8.6	3.4	11.0	34.1	21.9
Wet	0.4	9.2	11.3	5.6	7.4	2.8	20.7	3.7
	0.5	9.3	10.9	9.9	7.7	2.6	23.4	2.3
	0.6	15.5	12.1	7.6	5.4	1.4	38.2	16.2

Columns A & D: Mass loss (%) of low temperature hydrates (LTH) i.e. CSH gel and AF(t, m) phases recorded between 20 and 200°C. Note: no correction for background drift.

Columns B & E: $Ca(OH)_2$ content determined from the mass loss between 475-556°C for control samples and 490-527/566°C for wet/dry treated samples. Note: in column E the figure has been corrected for CO_2 mass uptake in order that direct comparison with column B can be made.

Columns C & F: $CaCO_3$ content determined from mass loss between 700°C and the clearly defined peak end temperature (average 823°C control samples, 896°C treated samples).

Column G: $CaCO_3$ content of treated sample not accounted for by conversion of $Ca(OH)_2$ or incidental pre-treatment carbonation and given by F-[(B-E) × (100/74) + C].

any event the change in magnitude of the endotherms suggests that only a small amount of $Ca(OH)_2$ is being converted to $CaCO_3$. The results of a quantitative analysis of the TG traces for the OPC pastes are given in Table II. Details of the calculations are given as a footnote to the table. The analysis confirmed that significant amounts of $Ca(OH)_2$ remained after treatment, cf. columns B and E. Column G gives the $CaCO_3$ content of the treated samples which cannot be accounted for by the partial conversion of $Ca(OH)_2$ and incidental pre-treatment carbonation. For all three w/c this represented about 65% of the $CaCO_3$ formed.

The lack of pronounced DTA endotherms between 100 and 200°C, for the control samples, shows that the drying process has resulted in some dehydration of CSH gel and AF(t, m) phases [11]. In the carbonated samples the DTA traces suggest a small endotherm, although its presence was not confirmed by the TG analysis.

The DTA traces for the synthetic pastes are shown in Fig. 2. The dry treated samples generally confirmed the features observed for the OPC specimens, namely partial dehydration of CSH gel etc. by the drying process, formation of $CaCO_3$ with little depletion of $Ca(OH)_2$ and the temperature shift of the $Ca(OH)_2$ endotherm. However, a clear endothermic effect below 200°C was now seen in the carbonated samples. Analysis of the TG traces for the synthetic paste are given in Table III. In this case the analysis showed that conversion of $Ca(OH)_2$ was less than 10%, and that 84% of the $CaCO_3$ must have been formed via carbonation of other material. The formation of a gel phase during carbonation, suggested by DTA, was confirmed by TG since the mass loss below 200°C changed from 2.6% in the control sample to 6.7% in the treated sample.

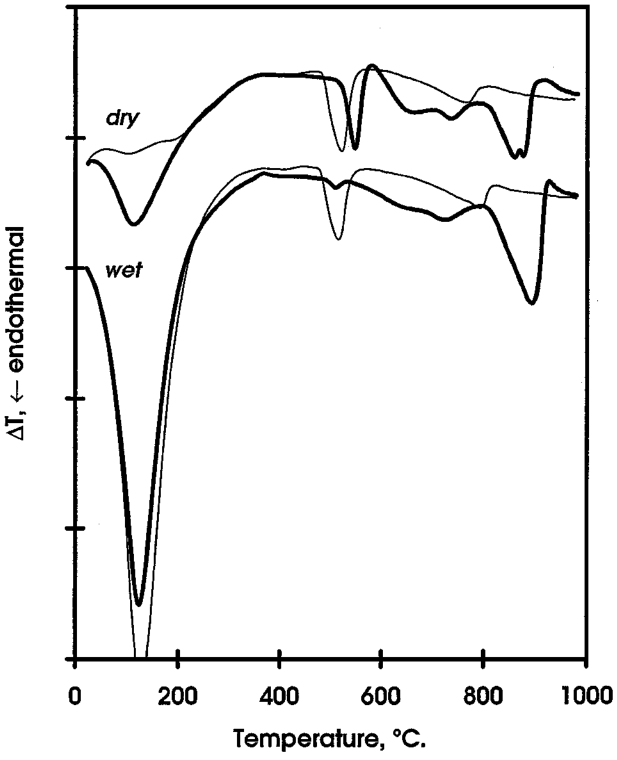

Figure 2 DTA thermograms, synthetic samples. Fine line: control samples, bold line: carbonated samples.

TABLE III Quantitative analysis of TG traces for the C_3S/C_2S pastes

	A	B	C	D	E	F	G
	Control			Treated			
	TG % LTH	%w/w $Ca(OH)_2$	%w/w $CaCO_3$	TG% LTH	%w/w $Ca(OH)_2$	%w/w $CaCO_3$	%w/w
Dry	2.6	8.4	4.1	6.7	7.7	30.0	25.0
Wet	26.3	6.0	4.8	18.7	0.9	38.8	27.2

3.1.2. *X-ray diffraction*

XRD (Table IV) confirmed that significant amounts of $Ca(OH)_2$ were still present in the samples after treatment. There was some qualitative evidence that the $Ca(OH)_2$ peaks were sharper after treatment. However, higher resolution XRD studies would be required to confirm the carbonation of crypto-crystalline material as suggested by examination of the DTA results. XRD also indicated that, in the OPC pastes, C_3S and C_2S were virtually eliminated during carbonation, which suggests that they are the most likely source of the

TABLE IV Comparison of XRD peak heights (counts per second)

		Wet								Dry							
		Control				Treated				Control				Treated			
		OPC			Syn	OPC			Syn	OPC			Syn	OPC			Syn
	2θ w/c	0.4	0.5	0.6	0.6	0.4	0.5	0.6	0.6	0.4	0.5	0.6	0.6	0.4	0.5	0.6	0.6
C_3S/C_2S	32.2	13	12	10	32	6	3	—	6	20	13	7	36	4	—	2	8
	41.2	3	4	5	13	3	—	—	3	6	5	5	16	—	—	—	4
	32.7	8	13	12	27	m	3	—	m	16	9	10	31	—	—	2	m
C_3S	51.6	3	2	4	—	3	2	m	—	4	3	4	—	—	—	—	—
	38.8	2	1	2	—	1	—	—	—	—	1	—	—	m	m	m	m
	30.1	5	4	5	—	—	—	—	—	6	4	4	—	m	m	m	m
C_2S	45.8	—	2	2	8	—	m	m	2	—	—	—	9	—	—	—	2
	31	3	2	4	9	—	—	—	—	4	4	2	10	—	—	—	3
	37.4	—	—	—	5	—	—	—	2	—	—	—	6	—	—	—	2
CH	34.1	32	29	34	21	17	5	8	4	36	36	33	17	23	21	24	8
	18.1	19	28	44	12	10	3	7	5	33	25	30	21	13	16	25	18
	50.7	8	7	8	6	4	—	—	—	10	8	6	6	5	6	6	4
	28.7	7	6	7	2	5	4	3	3	8	8	7	5	9	6	6	5
CCc	29.4	9	8	12	13	27	34	60	67	13	9	11	9	69	52	64	65
	48.7	—	—	—	—	5	8	9	12	—	—	—	—	15	8	9	11
	39.3	—	—	—	—	5	5	9	12	—	—	—	m	12	8	10	13
	43.3	—	—	—	—	4	4	8	m	—	—	—	—	10	8	9	10
CCa	26.2	—	—	—	—	—	3	7	8	—	—	—	—	—	—	—	—
	45.8	—	—	—	—	—	3	5	4	—	—	—	—	—	—	—	—
	27.2	—	—	—	—	—	4	6	m	—	—	—	—	—	—	—	—
	37.9	—	—	—	—	—	3	3	3	—	—	—	—	—	—	—	—
CCv	27.1	—	—	—	—	—	—	6	19	—	—	—	—	—	—	—	9
	32.8	—	—	—	—	—	—	5	19	—	—	—	—	—	—	—	9
	50.1	—	—	—	—	—	—	—	10	—	—	—	—	—	—	—	4
	24.9	—	—	—	—	—	—	—	11	—	—	—	—	—	—	—	6
Ett	9.1	7	9	11	—	5	—	5	—	—	—	—	—	—	—	—	—
	15.8	4	5	5	—	3	—	2	—	—	—	—	—	—	—	—	—
	22.9	4	5	6	—	3	—	m	—	—	—	—	—	—	—	—	—
	35	3	3	4	—	—	—	m	—	—	—	—	—	—	—	—	—

Notes:
C_3S/C_2S: Peaks jointly attributable to both compounds.
CH: $Ca(OH)_2$
CCc: Calcite.
CCa: Aragonite.
CCv: Vaterite.
Ett: Ettringite.
-: not detected.
m: masked by another compound.
Syn: synthetic C_3S/C_2S mixture.

unaccounted $CaCO_3$. The $CaCO_3$ formed during treatment was always calcite. In the synthetic pastes, the anhydrous material was also depleted although not always completely. As with the OPC pastes significant amounts of $Ca(OH)_2$ remained, confirming the TG results. As well as calcite, some vaterite was detected in the carbonated samples.

3.1.3. Mercury intrusion porosimetry

The pore size distribution curves for samples of w/c 0.4, 0.5, 0.6 OPC pastes are shown in Fig. 3a–c, respectively. The control samples of dry pastes with w/c 0.6 and 0.5 both had an initial pore entry diameter of about 1.0 μm , whilst that for the 0.4 w/c paste was an order of magnitude lower at about 0.1 μm. The total porosities were 0.33, 0.27, 0.17 cc g^{-1}, for pastes of w/c 0.6, 0.5, 0.4 respectively.

For the dry samples after carbonation the initial pore entry diameters were similar to those of the controls, suggesting that carbonation was not causing segmentation of the capillary pores. However, the total porosities were considerably reduced to 0.15, 0.10 and 0.04 cc g^{-1}, for pastes of w/c 0.6, 0.5, 0.4 respectively.

3.2. Wet samples

3.2.1. Differential thermal/thermogravimetric analyses

Typical DTA thermograms for pastes of w/c 0.4, 0.5, 0.6 which were wet (control) and then carbonated are shown in Fig. 4. As with the dry samples large quantities of $CaCO_3$ were formed during treatment, but in contrast to the behaviour of the dry samples there was a corresponding $Ca(OH)_2$ depletion. In samples of w/c 0.4 and 0.5, the treatment did not cause depletion of the gel/AF(t, m) phases, whereas in samples of w/c 0.6 a significant depletion was observed. The $CaCO_3$ endotherm in these latter samples was correspondingly larger. The DTA trace for the synthetic paste, Fig. 2, shows similar features to that of the OPC, w/c 0.6, paste.

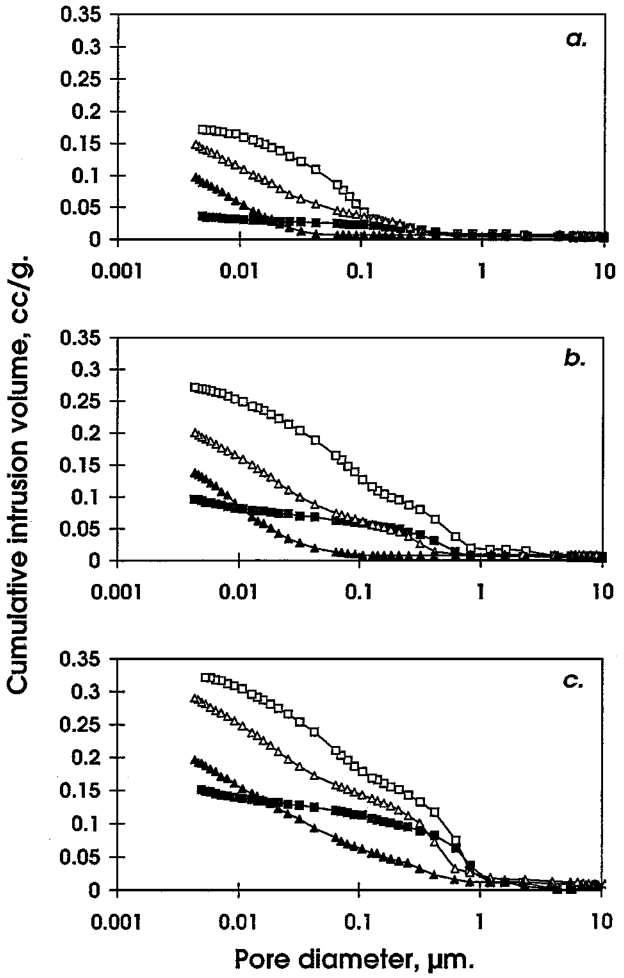

Figure 3 MIP pore size distribution curves; □ = dry control, Δ = wet control, ▲ = wet carbonated, ■ = dry carbonated. (a) w/c = 0.4; (b) w/c = 0.5; (c) w/c = 0.6.

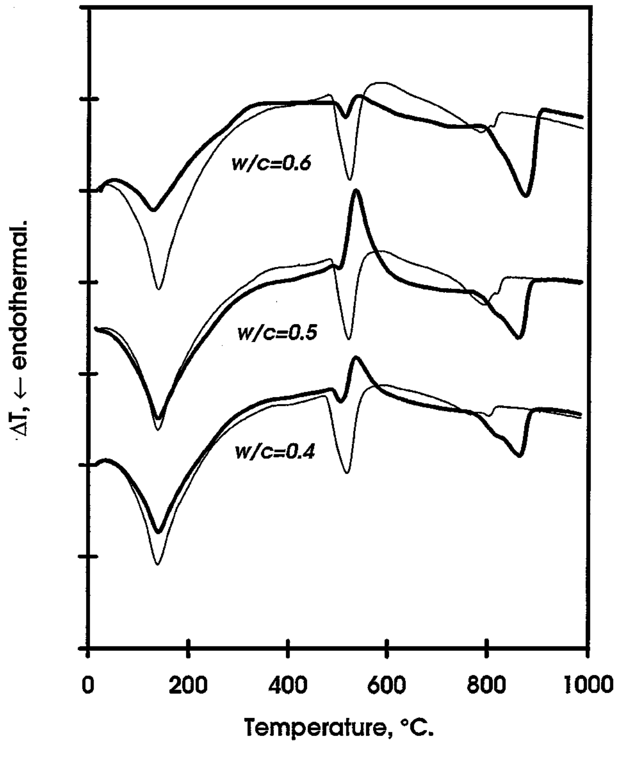

Figure 4 DTA thermograms, wet OPC samples. Fine line: control samples, bold line: carbonated samples.

DTA thermograms for the wet carbonated pastes of 0.4 and 0.5 w/c displayed a substantial exotherm immediately after the $Ca(OH)_2$ dehydroxylation endotherm. This exotherm was not accompanied by any perturbation in the TG traces, suggesting a structural transformation of one of the phases. Crystallisation of any gel phase produced [12] is unlikely since various synthetic standards did not exhibit a similar exotherm. Transitions involving aragonite or vaterite to calcite are also unlikely since several investigators [10,13] have shown that these are weakly endothermic and occur at around 450°C. It is possible that dehydroxylation results in the formation of amorphous CaO which then inverts to a crystalline form in a way similar to that found in $Mg(OH)_2$ containing minerals [13]. This is supported by the observation that the exotherm was not present in themograms of 0.6 w/c treated paste where there was virtually no $Ca(OH)_2$ after treatment, see Table II.

Quantitative analyses of the TG traces are given in Table II. In contrast to the behaviour of the dry treated samples, significant conversion of the $Ca(OH)_2$ has now occurred. For 0.4 and 0.5 w/c wet-treated pastes, less than 20% of the $CaCO_3$ remained unaccounted for by conversion of the $Ca(OH)_2$ and incidental pretreatment carbonation. In w/c 0.6 wet-treated samples, rather more $CaCO_3$ was formed and over 40% of it remained unaccounted for, despite almost total conversion of the $Ca(OH)_2$. In these samples, the extra $CaCO_3$ was, at least, partially formed from carbonation of the CSH gel, of which significant depletion was observed. Analysis of the TG traces for the synthetic pastes are given in Table III. In the wet-treated samples, $Ca(OH)_2$ was almost totally converted to $CaCO_3$. The conversion of CSH gel was quantitatively confirmed, but was probably not sufficient to account for all the remaining $CaCO_3$.

3.2.2. X-ray diffraction

XRD indicated that the unhydrated calcium silicate minerals were significantly depleted by treatment, the degree of depletion increasing with increasing w/c ratio. In the 0.6 w/c pastes, C_3S and C_2S were reduced to trace quantities.

In the wet-treated samples, only calcite was observed at w/c 0.4, calcite and aragonite were observed at w/c 0.5 and all three $CaCO_3$ polymorphs were observed at w/c 0.6. The degree of carbonation in general appeared to increase with w/c ratio and was much greater in the w/c 0.6 samples, as indicated by DTA/TG. It is interesting to note that ettringite frequently survived the $scCO_2$ treatment.

Wet-treated synthetic samples displayed almost complete depletion of both anhydrous material and $Ca(OH)_2$. Calcite, aragonite and vaterite were all detected, with the vaterite being significantly more abundant than in the OPC pastes with w/c 0.6 or the dry carbonated synthetic samples.

3.2.3. Mercury intrusion porosimetry

The pore size distribution curves for samples of w/c 0.4, 0.5, 0.6 OPC pastes are shown in Fig. 3a–c, respectively.

The control samples of pastes with w/c 0.6 and 0.5 both have an initial pore entry diameter of about 0.8 μm, whilst that for the w/c 0.4 paste is a little lower at about 0.5 μm. The total porosities are 0.29, 0.20, 0.15 cc g^{-1}, for w/c 0.6, 0.5, 0.4 pastes respectively.

For the wet samples after carbonation the initial pore entry diameter for the 0.6 w/c paste is about the same whilst for the 0.5 and 0.4 w/c pastes it is reduced to about 0.1 and 0.05 μm respectively. Thus in this case at w/c 0.5 and 0.4 the carbonation reactions are apparently causing some segmentation of the capillary pores. The total porosities are reduced to 0.20, 0.14 and 0.10 $cm^3\ g^{-1}$, for w/c 0.6, 0.5, 0.4 pastes respectively, which are not quite as low as those of the carbonated dry samples.

4. General discussion

Natural carbonation of cementitious materials requires the dissolution of atmospheric CO_2 in the pore water, to yield a mixture of H_2CO_3 , HCO_3^- and CO_3^{2-} species whose equilibrium concentrations are governed by the pH [14].

The principal reaction then involves dissolution of $Ca(OH)_2$ followed by nucleation and precipitation of $CaCO_3$, Equation 1, although the nature of the ions in solution and any intermediate steps in the reaction may be complex.

$$Ca(OH)_2 + CO_2 + H_2O = CaCO_3 + 2H_2O \qquad (1)$$

Carbonation of other compounds present is also possible, particularly the CSH gel, which may react to give $CaCO_3$ and SiO_2 gel.

With fresh pastes and high concentrations of CO_2 the hydration process is greatly accelerated [12, 15, 16]. Initially $CaCO_3$ and CSH gel are produced, Equation 2a, the latter being thought to resemble that formed during conventional hydration. No $Ca(OH)_2$ is produced. Subsequently the CSH gel is carbonated, causing de-calcification, ultimately leaving a hydrous SiO_2 gel, Equation 2b. When only limited water is available, little or no CSH gel is detected and reaction may be viewed as in Equation 2c [12]. Di-calcium silicate reacts in a similar fashion. However, these reactions are probably an oversimplification and their exact nature and extent will depend on the specific reaction parameters.

$$\begin{aligned} &3CaO{\cdot}SiO_2 + (3-x)CO_2 + yH_2O = \\ &\qquad xCaO{\cdot}SiO_2{\cdot}yH_2O + (3-x)CaCO_3 \qquad (2a) \\ &xCaO{\cdot}SiO_2{\cdot}yH_2O + xCO_2 \\ &\qquad = SiO_2{\cdot}yH_2O + xCaCO_3 \qquad (2b) \\ &3CaO{\cdot}SiO_2 + 3CO_2 + yH_2O \\ &\qquad = SiO_2{\cdot}yH_2O + 3CaCO_3 \qquad (2c) \end{aligned}$$

Under the conditions in the pressure vessel, the CO_2 is a supercritical fluid and behaves like a dense gas. In most processes it is simply used as an environmentally benign solvent where e.g. diffusivities of the reactants are such as to facilitate formation of the desired products. In the present case the $scCO_2$ acts as a solvent for water, although the solubility is not very high $\sim$1 g l^{-1} [8]. In addition the CO_2 is a major reactant, although the actual reacting species is not known with any confidence.

4.1. Dry samples

The $scCO_2$ plus dissolved water diffuses into the pore system of the cement paste. In the case of $Ca(OH)_2$ the results suggest that only finely divided or poorly crystalline material was being carbonated. It may be that there is not enough water for the conventional dissolution and precipitation mechanism described by Equation 1. With well crystalline material it is possible that reaction occurs, but only in a condensed film of surface moisture [17]. The $CaCO_3$ produced under these circumstances then acts as a barrier to further dissolution of calcium ions. However, with the poorly crystalline material there is probably a much greater surface area for reaction and it is easier to de-hydroxylate [17]. Phenolphthalein sprayed fracture surfaces failed to turn pink despite the $Ca(OH)_2$ content indicated by DTA/TG and XRD. It is possible that the formation of an impermeable skin around the $Ca(OH)_2$ crystals prevents the penetration of the phenolphthalein solution thus indicating complete carbonation.

Evidence from XRD suggests that $CaCO_3$ was formed from unhydrated material e.g. C_3S. In view of the limited amount of water available it is proposed that the likely reaction is similar to that given by Equation 2c. There is some evidence for the formation of a silica gel in the case of C_3S/C_2S pastes as suggested by the DTA/TG endotherms below 200°C, although these effects are not readily apparent in the commercial cements.

With regard to grc, long periods of natural weathering may cause the protective skin around the $Ca(OH)_2$ crystals to break-down and allow the release of calcium ions into the pore solution. If this were the case then the pH may be expected to increase and the problems of glass degradation might re-appear.

4.2. Wet samples

Since the CO_2 is in the super-critical state it is able to diffuse rapidly into the water saturated pores. At the temperature and pressure used, the resultant pore solution pH is considered to be around 3.0 [18]. This will accelerate dissolution of $Ca(OH)_2$ and since there is sufficient water, the reaction should proceed as in Equation 1.

Again carbonation of C_3S has occurred but this time with a difference. It has been eliminated in pastes of w/c 0.6 but not in those of w/c 0.4 and 0.5. In the latter cases the formation of carbonation products results in gradual segmentation of the capillary pores leading to reduced access of the $scCO_2$.

With regard to grc application there is now no $Ca(OH)_2$, and with carbonation of C_3S/C_2S the potential for further production of $Ca(OH)_2$ has been removed. Therefore the pH of the matrix should remain low throughout its lifetime. The porosity of the matrix has been much reduced, especially the pore entry diameters which will probably reduce the mobility of aggressive species.

It should be emphasised that the reactions discussed relate to quite specific carbonation conditions and there are many variables that may well be of importance. In the case of the matrix these include w/c, cement type, aggregates, admixtures and hydration parameters. On the processing side, variables include partial pressure of the CO_2, temperature, time, and whether a static or dynamic procedure is used.

5. Conclusions

(1) Carbonation of hydrated cements was greatly accelerated in a $scCO_2$ environment and the nature of the reactions was dependent on the amount of water present in the hardened cement paste.

(2) In the case of samples which were pre-dried prior to carbonation the reaction was independent of w/c and resulted in the conversion of all the remaining C_3S/C_2S and marginal conversion of $Ca(OH)_2$, to calcium carbonate in the form of calcite.

(3) In contrast, samples which were equilibrated at 95% RH carbonated via a different mechanism which was dependent on the w/c. Thus at a w/c of 0.6 all the C_3S/C_2S, most of the $Ca(OH)_2$ and a significant amount of the CSH gel were converted to calcium carbonate which was now present as calcite, vaterite and aragonite. At a w/c of 0.4 and 0.5 most of the $Ca(OH)_2$ but only small amounts of anhydrous calcium silicate minerals and CSH gel were converted to calcium carbonate which was present mainly as calcite. The difference in behaviour was attributed to the more open pore structure found in pastes made with a w/c 0.6 compared to that found in pastes made with w/c of 0.4 & 0.5.

(4) During the carbonation treatment, the pore structure of the cement paste was altered and it was possible to obtain substantial reductions in the initial pore entry diameter and total porosity.

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