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The microstructure and strength of carbonated aluminous cements

B. M. HENRY, B. A. KILMARTIN, G. W. GROVES
Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK

The effect of carbonation on the microstructure and flexural strength of hardened aluminous cement pastes has been investigated. It is found that pastes containing either C_3AH_6* or CAH_{10} as the major crystalline hydrate phase are readily partially carbonated at a humidity of 72.6%. The carbonation products are calcite, vaterite, which is present as 50 nm crystallites, and hydrous alumina, which is always produced in the form of an amorphous gel. Partial carbonation produces a modest increase in the flexural strength for pastes containing either C_3AH_6 or CAH_{10}.

1. Introduction

Both calcium silicate based cements (e.g., ordinary Portland Cement, OPC) and calcium aluminate based cements react with atmospheric carbon dioxide when in the hardened state, under appropriate conditions of humidity. This phenomenon has been extensively studied in the case of OPC, where the loss in alkalinity accompanying the reaction can lead to the corrosion of reinforcing steel which has insufficient concrete cover. The reaction in this case leads ultimately to the formation of calcium carbonate and silica gel but the kinetics of the reaction are complicated since they depend on the process of CO_2 gas diffusing through empty pores and reacting in solution-filled pores [1]. The balance between solution-filled and empty pores depends on both the size of the pore structure and the relative humidity of the atmosphere with which the cement paste is in equilibrium. Carbonation does not occur when the humidity is low enough to empty all the pores but also it is very slow when all the pores are solution-filled so that rapid penetration of CO_2 through empty pores cannot occur. The same basic effects of pore structure and humidity can be expected to occur in the carbonation of aluminous cements, in which the final products should be calcium carbonate and some form of hydrated alumina. However the carbonation of aluminous cements has been much less studied than that of OPC.

In particular, whereas the detailed microstructure of partially carbonated OPC and tricalcium silicate pastes have been studied by transmission electron microscopy (TEM) and ^{29}Si nuclear magnetic resonance (NMR) [2, 3] the changes in the microstructure of aluminous cements due to carbonation are not known in detail. Perez *et al.* [4] and Perez– Mendez and Trivino-Vazquez [5] have reported a study of the strength developed by stable carbonated phases in high alumina cement mortars. They found that the decrease in strength occurring when the hexagonal hydrates CAH_{10} and C_2AH_8 which form at lower temperatures convert at higher temperatures to the denser cubic hydrate C_3AH_6, can be compensated for by an increase in strength occurring when C_3AH_6 is carbonated. However, they did not report on the effect of directly carbonating the CAH_{10} phase. The purpose of the present paper is to report on the microstructures of carbonated hardened aluminous cements as seen by TEM and to investigate the effect of carbonation on the tensile strength of pastes containing either CAH_{10} or C_3AH_6.

2. Experimental procedure

The cements used were a Secar 71 and a Ciment Fondu produced by the Lafarge Company. The analysis for the batches used were kindly supplied by the Lafarge Company and are given in Table I. Cement pastes were mixed to a water:cement ratio of 0.4 and cast into cylindrical polythene sample tubes of 13 mm internal radius and length 45 mm. After sealing, the sample tubes were placed either in a refrigerator at 4 °C or in water baths at 25 or 40 °C for a period of hardening. After a fixed period the sample tubes were cut open to release the hardened cement paste cylinder, which was then cut into slices of approximately 0.85 mm thickness, using a water-lubricated slow speed diamond saw. Slices to be carbonated were placed in a chamber containing a saturated solution of ammonium chloride and potassium nitrate, giving a humidity of 72.6%. Either CO_2 gas, or air, was trickled through the chamber to produce the carbonation. Prior to the carbonation treatment slices of hardened paste were conditioned by soaking in distilled water for 3 to 4 h and then transferring them to the chamber containing the solution co-saturated with ammonium chloride and potassium nitrate where they were left for 24 h before the admission of CO_2, in order to allow their water content to reduce until it was in

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*Cement chemist's abbreviation notation is used: thus $C = CaO$, $A = Al_2O_3$, $H = H_2O$, $C_3AH_6 = 3CaO.Al_2O_3.6H_2O$.

TABLE I Chemical composition (wt %) of Secar 71 and Ciment Fondu

	Al_2O_3	CaO	SiO_2	Fe_2O_3	MgO	Na_2O	K_2O
Secar 71	70.2	28.3	0.30	0.1	0.12	0.23	0.01
Ciment Fondu	38.0	38.1	4.6	15.2	0.32	0.04	0.09

equilibrium with the 72.6% humidity atmosphere. The purpose of this was to equilibrate the pore structure with the control humidity prior to carbonation, particularly in the case of the rapid carbonation in pure CO_2. The progress of the carbonation reaction was assessed by X-ray diffraction from a slice mounted in a Philips diffractometer.

Mechanical testing was performed directly on the disc-shaped slices by means of the ball and ring test in which a ball is pressed onto the centre of the disc which is supported by a ring at its edge [6]. The disc fails under biaxial bending stress so that the failure load gives a (tensile) flexural strength measurement. The advantages of this type of test are the minimal sample preparation required and the smallness of the sample, so that at least 16 test results could be obtained from the slices cut from the contents of a single sample tube.

Specimens for examination in the TEM were prepared from slices by grinding, followed by ion-beam thinning, as described elsewhere [7].

3. Results and discussion

3.1. Progress of carbonation

3.1.1. Samples containing C_3AH_6

Secar pastes hydrated for 7 days at 40 °C to produce C_3AH_6 showed rapid initial carbonation in CO_2. After 3 h for example substantial quantities of calcite and vaterite are detected. In air carbonation, a period of 8 days produced rather less carbonation than 3 h in CO_2, with a higher proportion of vaterite (Fig. 1). Abrading the surface of the slice carbonated in CO_2 reduced the intensity of the calcite reflections but left the vaterite peaks unchanged, suggesting that vaterite is formed more at an early stage and calcite at a later stage of carbonation (Fig. 2).

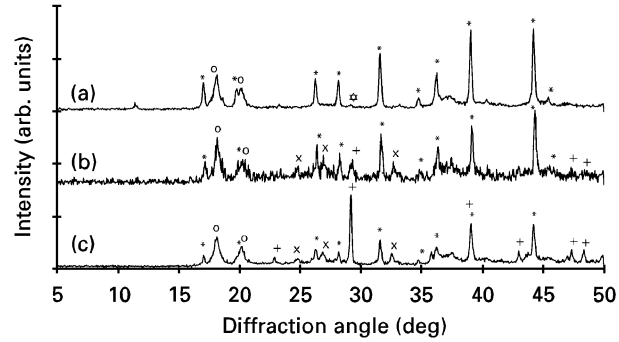

Figure 1 X-ray diffraction spectra of carbonated and uncarbonated samples containing C_3AH_6. (a) As prepared, (b) 8 days in air and (c) 3 h in CO_2. Key: (∗) C_3AH_6, (○) AH_3, (+) calcite, (×) vaterite and (⁎) CAH_{10}.

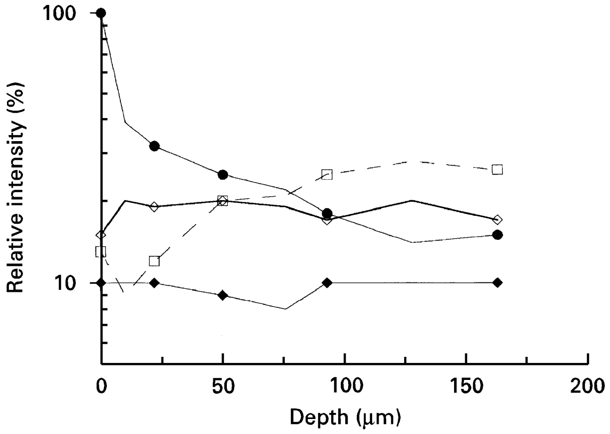

Figure 2 Carbonation of C_3AH_6 as a function of sample depth. Key: (◇) AH_3, (●) CC, (□) C_3AH_6 and (◆) vaterite.

The rate of carbonation is indicated by X-ray diffraction spectra slowed markedly after the initially rapid stage. For example between 10 and 31 days in air the intensities of the C_3AH_6 reflections showed little further decrease. An initially very rapid partial carbonation followed by a period of much slower further carbonation has also been reported for tricalcium silicate cement pastes carbonating in CO_2 under the same conditions as in the present study [8]. The cause of the dramatic reduction in carbonation rate may be similar in both cases, namely, interference by the products of carbonation. It should be noted that it is not necessary for the pore structure to be completely filled by reaction product in order for the rate of penetration of CO_2 to be drastically reduced. If the pore size is reduced to the level at which further capillary condensation at the constant prevailing humidity reduces the percolation of gas-filled pores there will be a corresponding reduction in the rate of penetration of CO_2. It was notable that the intensity of the AH_3, gibbsite, reflections showed no significant increases throughout the entire period of carbonation, suggesting that the hydrated alumina formed as a result of the reaction of the C_3AH_6 with CO_2 was in an amorphous form.

The amorphous nature of the hydrated alumina formed by carbonation was confirmed in a Ciment Fondu specimen carbonated in CO_2 for 5 days. Although only a trace of C_3AH_6 remained, no gibbsite could be detected by X-ray diffraction. (In this specimen, C_3AH_6 was the only crystalline hydrated phase present after curing for 7 days at 40 °C prior to carbonation).

3.1.2. Samples containing CAH_{10}

Secar hydrated at 5 °C for 7 days to produce CAH_{10} carbonated in a similar way to samples containing C_3AH_6, with, if anything, a slightly more rapid rate of carbonation as indicated by X-ray diffraction. Again, the production of gibbsite was not detected.

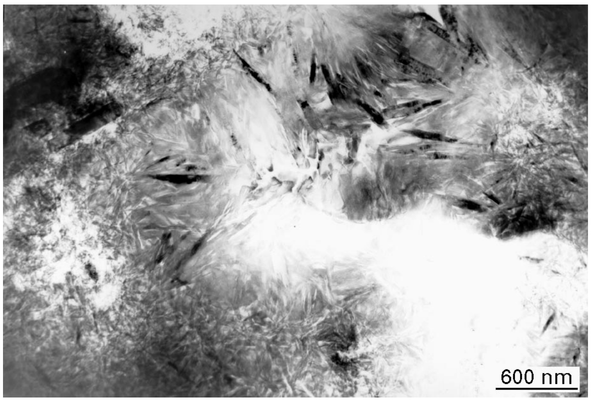

Figure 3 Laths of crystalline gibbsite surrounded by amorphous gel in a specimen hydrated at 40 °C for 7 days.

3.2. Microstructures of carbonated pastes

A major point of interest in the microstructure of a hardened, uncarbonated Secar paste hydrated at 40 °C to produce C_3AH_6, is the nature of the hydrated alumina phase which must present. Fig. 3 shows a region of such a specimen in which laths of crystalline gibbsite can be seen to be embedded in a matrix of an amorphous gel. Microanalysis of the gel showed that it was a nearly pure alumina gel. It is not certain whether the mixture of gibbsite and amorphous gel represents the original hydration product or is the result of a subsequent partial crystallization of the amorphous phase.

Fig. 4 (a and b) shows a region of the Secar paste hydrated at 40 °C for 7 days and then carbonated for 3 h in CO_2. The bright field/dark field pair, the dark field micrograph being taken with reflections from crystalline vaterite, shows a very intimate mixture of vaterite crystallites ~ 50 nm in size embedded in a fine-textured alumina gel. The distribution of vaterite particles is not uniform – there is a suggestion that it outlines a region of gel which could have been the original site of a C_3AH_6 crystal. No crystalline gibbsite is visible in the region. The morphology of the amorphous alumina is quite similar to that of the alumina gel in the uncarbonated specimen (Fig. 3).

Similar mixtures of small vaterite crystallites and alumina gel were found in a Secar specimen carbonated after being hydrated at low temperature to produce CAH_{10}, as can be seen in Fig. 5 (a and b). Another region of this specimen, Fig. 6, showed residues of CAH_{10} plates (CAH_{10} rapidly loses its crystallinity in the electron beam) and alumina gel, but no carbonate could be found in this area. This presumably is a region not yet carbonated, in which alumina gel has arisen from the hydration of some of the CA_2 phase present in Secar 71.

In carbonated specimens containing initially either C_3AH_6 or CAH_{10}, finely dispersed carbonate crystallites were found from their electron diffraction patterns to be vaterite. The only positively identified calcite region was in the form of a relatively large crystal. X-ray diffraction indicated the presence of substantial amounts of calcite in all cases, but the calcite was probably under-represented in the TEM observations because of being present as larger crystals, which do not thin as well during TEM specimen preparation by ion-beam milling as do mixtures of gel and very small crystallites. A discrepancy between the frequency of observation of vaterite relative to calcite in TEM observations compared to the relative intensities of the corresponding X-ray reflections has been noted previously in studies of carbonated silicate cement pastes [8]. The vaterite/gel mixtures observed in carbonated aluminous cements are indeed somewhat similar to those observed in carbonated silicate cements with, of course, alumina gel taking the place of silica gel.

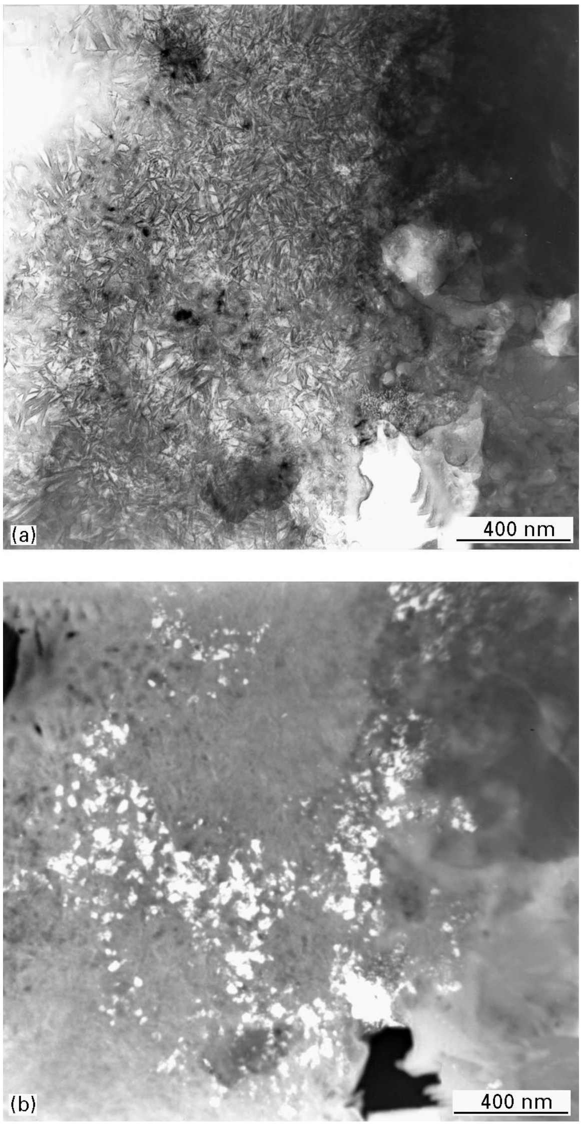

Figure 4 (a) A bright field and (b) dark field image of a region featuring vaterite crystals in a Secar paste hydrated at 40 °C for 7 days and then carbonated for 3 h in CO_2.

3.3. The flexural strength of carbonated pastes

Tensile strengths as measured by the "ball and ring" test are presented in Table II. The carbonation treatment was in each case a period of 3 days in CO_2, immediately following the curing treatment. In Table II, the error figures refer to the estimated standard deviation of the mean of 16 values. The curing treatments were chosen to give a substantial degree of hydration, but X-ray diffraction from a sample from each batch showed that some CA, or in the case of Secar, CA and CA_2, remained after the curing treatment. As expected, the cements cured at 4 °C contained CAH_{10} and those cured at 40 °C, C_3AH_6, as the main crystalline hydrate phases. The carbonation treatment produced calcite and vaterite but carbonation was incomplete in all cases i.e., significant CAH_{10} or C_3AH_6 remained after the carbonation treatment.

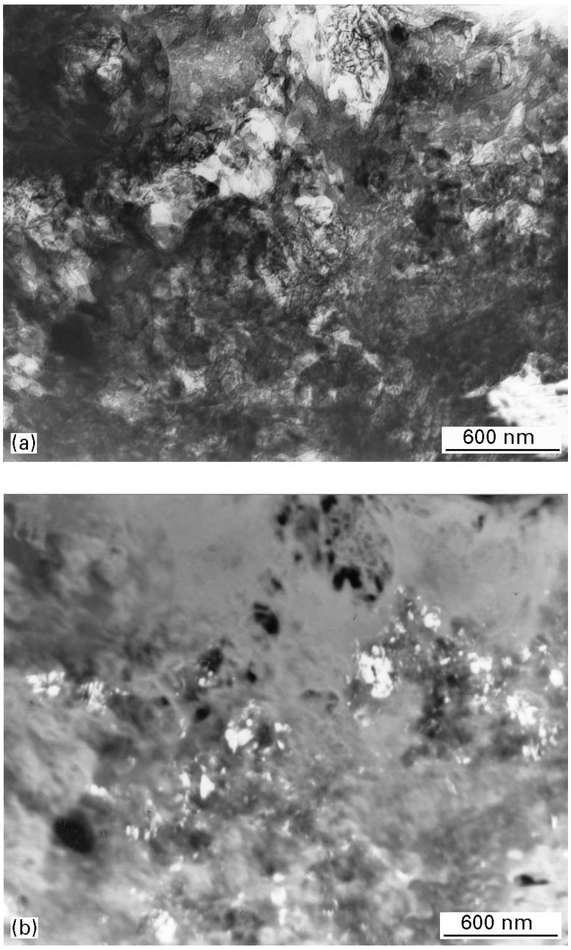

Figure 5 (a) A bright field and (b) dark field image showing crystalline vaterite and alumina gel in a Secar specimen hydrated at 4 °C for 7 days and then carbonated for 3 h in CO_2.

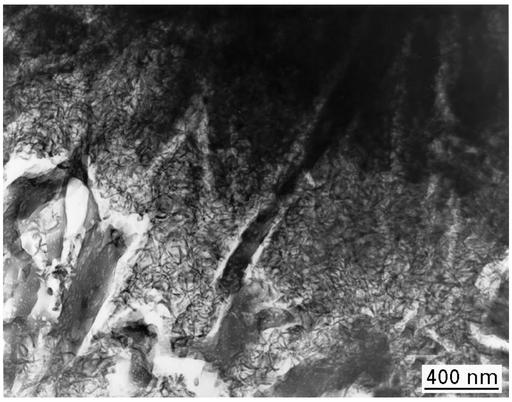

Figure 6 A bright field image featuring crystals of CAH_{10} embedded in alumina gel.

In all cases, the partial carbonation of the hardened pastes produced a modest increase in tensile strength. Although a small amount of additional hydration may have occurred during the carbonation treatment, the shortness of this period and the fact that the pastes were already relatively well hydrated suggests that the reaction products of carbonation were primarily responsible for the increase in strength. The magnitude, in a relative sense, of the increase in strength is comparable with that found by Perez–Mendez and Trivino-Vazquez [5] for high alumina cement mortars containing C_3AH_6 and subjected to similar curing and carbonation treatments, although the absolute level of flexural strength found in their case was significantly lower.

In discussions of the strength of high alumina cements and concretes much attention has focussed upon the hydrate phases which are present, through their influence on the porosity of the hardened paste, mortar or concrete. Thus it has been pointed out that the conversion reaction of CAH_{10} to C_3AH_6 leads to increased porosity owing to the smaller solid volume of the products of conversion [9]. It has been further suggested that crystallization of amorphous AH_3 to gibbsite is a factor in loss of strength [10]. From these points of view, the improvement of strength by carbonation of C_3AH_6 is readily explicable. In this case the reaction to give calcite plus gibbsite would lead to a solid volume increase of 17%, and the effective volume increase and consequent reduction in macroporosity must be greater than this because we have shown that the hydrated alumina resulting from carbonation at $\sim 20\,^{\circ}C$ is amorphous. The improvement in strength found when CA paste containing CAH_{10} is carbonated is less expected since in this case carbonation to give calcite and gibbsite would give a solid volume decrease of 43%. It seems unlikely that this could be overcome by further hydration even when assisted by water released by the carbonation reaction. The nature of the observed microstructure containing amorphous alumina gel reinforced by vaterite microcrystals may be of importance. It is not clear what effective solid volume the alumina gel should be considered to possess. The microporosity within it should not be classified with larger pores which can produce strength-limiting macro defects in the paste. In terms of providing the medium through which cracks must propagate in a tensile failure it is possible that the

TABLE II Tensile strengths of carbonated and uncarbonated samples of Secar 71 and Ciment Fondu

Cement type	Curing treatment	Uncarbonated strength MPa	Carbonated strength
Ciment Fondu	1 year at 4 °C	37.4 ± 0.9	41.5 ± 1.2
Secar 71	4 months at 4 °C	23.4 ± 1.5	28.8 ± 0.7
Climent Fondu	7 days at 40 °C	23.4 ± 0.8	26.9 ± 0.6
Secar 71	7 days at 40 °C	24.4 ± 1.2	27.3 ± 1.4

reinforced alumina gel has a higher crack propagation resistance than the CAH_{10} crystals which it replaces.

4. Summary and conclusions

1. Aluminous cement pastes containing either CAH_{10} or C_3AH_6 are readily carbonated, though under constant humidity conditions the rate of carbonation falls off rapidly with time.

2. The carbonate is in the form of calcite and vaterite, with the vaterite being present as very small crystallites, ~ 50 nm in size.

3. The hydrated alumina produced by the carbonation reaction at room temperature is in the form of an amorphous gel phase.

4. A 3-day period of carbonation in CO_2 produced a small increase in tensile strength in aluminous cements cured to give either CAH_{10} or C_3AH_6.

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