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GRADUAL TRANSFORMATION OF $Ca(OH)_2$ INTO $CaCO_3$ ON CEMENT HYDRATION

XRD study

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The low temperature of decomposition of some calcium carbonates and the bending of the TG curves of hydrated cement between 500 and 800°C suggested the presence of some complex compound(s), which needed complementary investigation (XRD, TG). Stepwise transformation of portlandite (and/or lime) into calcium carbonate, with intermediate steps of calcium carbonate hydroxide hydrates (CCH-1 to CCH-5), was indicated by the previous study of two OPC.

This was checked here on four cements ground for t_g=15, 20, 25 and 30 min and hydrated either in water vapour, successively at RH=1.0, 0.95 and 0.5 for 2 weeks each (WR1, WR2 and WR3, respectively) or as mortars in liquid water (1m), followed by WR as above. The d[001] spacing of portlandite was confirmed to vary: here between the lowest and the highest standard values. The diffractograms of n=32 different samples were analyzed for presence of standard CCH peaks, generally slightly displaced. These were: CCH-1 $[Ca_3(CO_3)_2(OH)_2]$: N=11 peaks, of three different $d[hkl]$ spacings, CCH-2 $[Ca_6(CO_{2.65})_2(OH_{657})_7(H_2O)_2]$: N=10 for two $d[hkl]$, CCH-3 $[Ca_3(CO_3)_2(OH)_2\cdot 1.5H_2O]$: N=14 for five $d[hkl]$, CCH-4, ikaite $[CaCO_3(H_2O)_6]$: N=13 for six $d[hkl]$, CCH-5$[CaCO_3(H_2O)]$: N=15 for five $d[hkl]$. Thus the most probable is the presence of the last three. The stepwise transformation of $Ca(OH)_2$ into $CaCO_3$ was confirmed:

$$\text{portlandite (varying } d[001])\rightarrow\text{CCH-1}\rightarrow\text{CCH-2}\rightarrow\text{CCH-3}\rightarrow\text{CCH-4}\rightarrow\text{CCH-5}\rightarrow CaCO_3$$

The content of CCH was the highest at t_{gr}=15 min, decreasing down to t_{gr}=25 min and increasing slightly at 30 min, as inferred from the number of the peaks observed. After cement powder hydration at RH=1.0 (WR1) peak number increased gradually from CCH-1 to CCH-5, whereas in the hydrated mortar (1m) the peak number decreased from CCH-1 to CCH-5, indicating the respective progress of the carbonation reaction.

Keywords: *calcium carbonates, calcium carbonates hydrates, calcium carbonate hydroxide, carbonation of portlandite, cement grinding, cement hydration, XRD*

Introduction

The decomposition of calcium carbonate at temperatures lower than the nominal ~900°C is known, e.g. [1]. Attention was paid in the recent study e.g. to determination of calcite forming with time at a given sampling depth of plasters and mortars [2, 3] and its influence on damage of concrete at a high temperature [4].

The unusually low temperature of decomposition of some calcium carbonates, the bending of the TG curve of hydrated cement, between 500 and 800°C (Fig. 1) and other observations suggest the presence of some complex compound(s). Supplementary study by XRD was needed to explain particular steps of carbonation reaction.

The increase in XRD basal spacings of portlandite, with ageing and with temperature, was found previously in two Indian OPC [5]. The hypothesis was suggested of CO_3^{2-} ions inclusion in the portlandite crystal lattice and its gradual transformation into calcium carbonate with intermediate steps of calcium carbonate hydroxide, hydroxide hydrates and hydrates [6]. Indeed three different species of calcium carbonate were identified by thermal IR/TG spectroscopy, and they were decomposing with CO_2 and water evolution, at temperatures lower than the nominal one for calcite [7].

These observations are checked here on four Spanish OPCs, ground for various times, hydrated in liquid water and/or in water vapour and studied by XRD. IR/TG and other methods were also applied and the results will be presented elsewhere.

Hydration of alite and belite (calcium silicates, as cement components) to portlandite proceeds in liquid water at a water cement ratio (w/c=0.4 to 0.5), resulting almost in a solid state system. There is even less free liquid water after ageing, when the portlandite has reacted with carbon dioxide from air, and possibly also with water vapour [7]. The system is almost in solid state thus reactions proceeding in solu-

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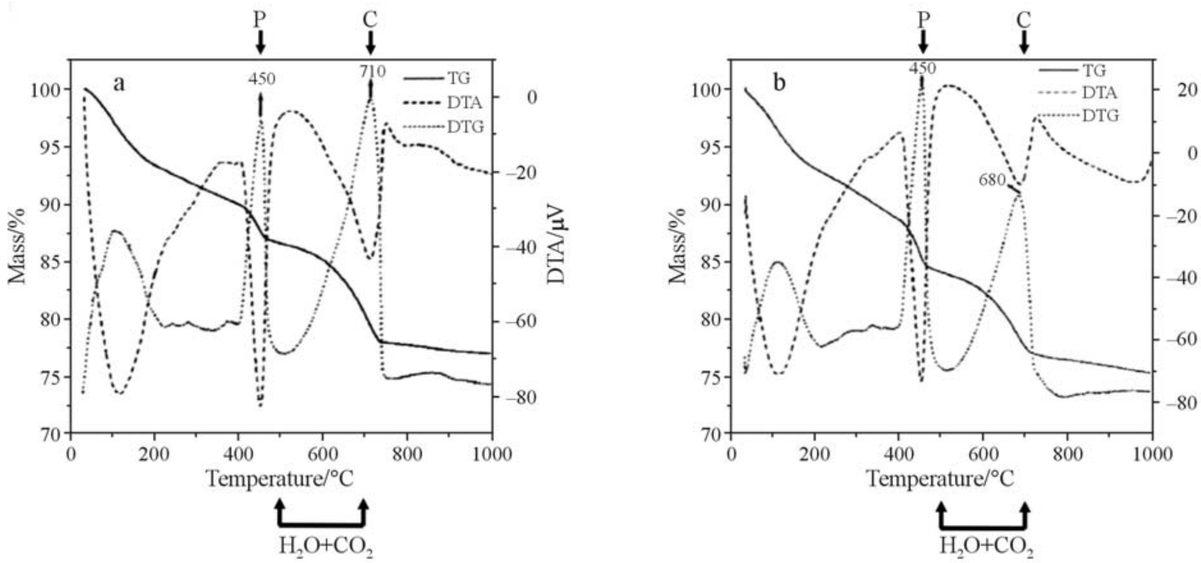

Fig. 1 Results of thermal analysis (DTA/DTG/TG) in argon of two pastes, a – one of a lower strength and b – another of a higher strength [4]

tion and/or suspension are not directly applicable, which is analyzed below.

The candidates for intermediate compounds between $Ca(OH)_2$ and $CaCO_3$

There are 9 standard XRD files of portlandite of varying basal spacings, Tables 1 and 2. This is most probably due to partial substitution of OH ions by bigger CO_3 ions, resulting in bigger basal spacings [5]. Carbonate formation may proceed by intermediate steps of calcium carbonate hydroxide hydrate, accommodating besides carbon dioxide, also water molecules, which in turn are gradually lost and pure (or almost pure) calcium carbonate results.

The candidates for these intermediate compounds were chosen basing on the analysis of standard XRD files and on the previous IR and TG study. Thermal IR spectra of the gases evolved from the aged cement pastes indicated three peaks of carbon dioxide escape, with maxima about 350, 630 and 850°C. The TG analysis and mass spectroscopy revealed the simultaneous escape of water [7]. The intermediate compounds may tend to stoichiometric composition: a fresh cement (OPC) from The Netherlands, studied previously, indicated a high increase in mass after heating at 220°C and cooling (both in air), showing a 'thirst' either for water or for carbon dioxide or for both [8]:

$$\Delta M(110°\mathrm{C})=8.2\%,\ \Delta M(220°\mathrm{C})=5.7\%,$$
$$\Delta M(\mathrm{rehydration})=21.8\%,\ \Delta M(400°\mathrm{C})=14.5\%$$

After ageing:

$$\Delta M(110°\mathrm{C})=6.8\%,\ \Delta M(220°\mathrm{C})=5.4\%,$$
$$\Delta M(\mathrm{rehydration})=?,\ \Delta M(400°\mathrm{C})=2.8\%$$

This was not observed in this aged specimen, but a small increase (1–2%) was frequently found about this temperature, when heated in air [5, 7]. TG analysis and mass spectroscopy (MS) revealed in aged hydrated cement, the gradual strong bonding of the adsorbed water (110°C), which after several years es-

Table 1 Compounds participating in the carbonation reaction, found in JCPDS-ICDD files

Portlandite	$Ca(OH)_2$	1-1079, 2-967, 2-968, 2-969, **4-733**, 44-1481, **1-72-156**, 1-87-673, 1-87-674
CCH-1	Calcium carbonate hydroxide: $Ca_3(CO_3)_2(OH)_2$	23-106 [9, 10]
CCH-2	Defernite: $Ca_6(CO_{2.65})_2(OH_{.657})_7(H_2O)_2$	1-78-1540 [11]
CCH-3	Calcium carbonate hydroxide hydrate: $Ca_3(CO_3)_2(OH)_2{\cdot}1.5H_2O$	23-107 [9, 10]
CCH-4	Ikaite: $CaCO_3(H_2O)_6$	7-416 [12–14]; 1-75-1733 [15]; 1-72-670 [14]
CCH-5	Monohydrocalcite: $CaCO_3(H_2O)$	22-147; 29-306 [16]; 1-83-1922; 1-83-1923 [17]; 1-84-49 [18];
Vaterite	$CaCO_3$	33-268
Aragonite	$CaCO_3$	41-1475
Calcite	$CaCO_3$	5-586

Table 2 Characteristics of the crystal structure of compounds participating in the gradual transformation of $Ca(OH)_2$ to $CaCO_3$

Mineral	System	*a*/Å	*b*/Å	*c*/Å	*d*[*hkl*]	Density	Volume of cell	File No.
Portlandite	Hexagonal	3.5853	3.5853	4.8950	4.895 [001] 3.105 [100]	2.26_c	54.49	1-72-156
Portlandite	Hexagonal	3.5899	3.5899	4.9160	4.922 [001] 3.111 [100]	2.24_c	54.87	44-1481
CCH-1	Unknown				4.670 ? 2.94 (I=1)			23-106
Defernite	Orthorhomb.	17.86	22.775	3.658	7.757 [020] 8.930 [200]	2.24_c 2.50_m	1487.93	1-78-1 -1540
CCH-3	Unknown				4.810 ? 2.732 (I=1)	1.82_m		23-107
Ikaite	Monoclin.	8.87	8.23	11.020	5.171 [002] 4.162 [200]	1.83_c	754.98	37-416
Ikaite	Monoclin.	8.792	8.310	11.021	5.161 [002] 4.117 [200]	1.83_c	754.07	1-75- -1733[1]
CCH-5	Hexagonal	6.092	6.092	7.534	2.510 [003] 5.260 [100]		242.15	22-147 →
		10.566	10.566	7.573	2.524 [003] 3.050 [300]	2.48_c 2.39_m	732.18	29-306
		10.554	10.554	7.5446	2.515 [003] 4.570 [200]	2.42_c 2.38_m	727.73	1.83. . .1923
		6.0931	6.0931	7.5446	2.515 [003] 5.277 [100]	2.42_c 2.38_m	242.57	1.83. .1922
Vaterite	Hexagonal	7.1473	7.1473	16.917	4.226 [004] 3.294[112]	2.66_c	748.41	33-268
Aragonite	Orthorhomb.	4.9623	7.9680	5.7439	2.872 [002] 3.397 [111]	2.93_c 2.95_m	227.11	41-1475
Calcite	Rhomboh.	4.989	4.9890	17.062	2.845 [006] 1.440 [300]	2.71_c 2.71_m	367.78	5-586

[1] Identical with 1-72-670

caped above 400°C, possibly from calcium carbonate hydroxide hydrates.

The most probable sequence of the reactions mentioned above is:

$$\text{Portlandite } (d[hkl]_{\min})\rightarrow\text{portlandite } (d[hkl]_{\max})]\rightarrow \text{calcium carbonate hydroxide} \rightarrow \text{calcium carbonate hydroxide hydrate}\rightarrow\text{calcium carbonate hydrate} \rightarrow \text{calcium carbonate} \tag{1a}$$

The query in the JCPDS-ICDD files (Table 1), indicated the following compounds characterized in the Table 2.

The samples CCH-1 and CCH-3 were observed in lime factory (Johann Schaefer Kalkwerke, Diez/Lahn) and studied by SEM [9, 10]. CCH-2 characteristics were calculated from ICSD powder data [11]. Ikaite crystals (CCH-4) were grown from calcium carbonate gels left for several months at 3–5°C in solutions containing 400 ppm of sodium polyphosphate [37–416], calculated from ICSD [1-72-670] or the specimen was from Bransfield Strait, Antarctica and its characteristics were calculated from ICSD [1-75-1733], [12–15]. Monohydrocalcite (CCH-5) was obtained from Lake Fellmongery, Robe, South Australia [29-306], substituting [22-147]; the characteristics for [1-83-1922] and [1-83-1923] were calculated from ICSD and the structure was derived [16–18].

Thus CCH-1 and CCH-3 proceed from lime hydration and its carbonation; the CCH-4 (ikaite) is a low temperature species, containing high amount of water (six molecules per one carbonate ion). Monohydrocalcite (CCH-5) is forming in solution or suspension. Formation of ikaite [$CaCO_3(H_2O)_6$] would explain the high increase in mass after heating at 220°C and cooling in air of a hydrated cement powder, mentioned above [8].

Geometrical considerations

The crystallographic data for the compounds presented above are indicated in Table 2. The *a* spacing seems to increase gradually from CCH-1 up to CCH-4 (ikaite) and then it decreases down to calcite, as the density changes in opposite direction: it is similar for portlandite, CCH-1 and CCH-2, it drops for CCH-4, due to a high content of crystal water in $CaCO_3·6H_2O$, and it increases at CCH-5, when most of this water is lost ($CaCO_3·H_2O$). It is higher and slightly variable in the three polymorphs of calcium carbonate, being the highest in the metastable aragonite, which nanocrystals indicated in HRTEM a high crystallinity [19].

Experimental

Materials

Cement powders and hydrated mortars were supplied by the cement plant accompanied by the data on chemical composition (Table 3), specific surface and compressive strength (Table 4).

Cement powders were obtained from clinker, ground in a ball mill for t_{gr}=15, 20, 25 and 30 min (4 series, CS-15, CS-20, CS-25 and CS-30). They were hydrated *(i)* as powders in water vapour at RH=1.0 (WR1), 0.95 (WR2) and 0.5 (WR3), for 2 weeks in each case, taking after each step a sample for XRD (total 12 samples) *(ii)* as mortars after mixing the cement powder with standard sand and formation of standard specimens. They were stored in liquid water for 28 days (4 samples, CS-15–1m, CS-20-1m, CS-25-1m and CS-30-1m), followed by storing in water vapour as above (12 samples).

Methods

XRD study was performed by the Siemens D-501 (CuK_α radiation) equipped with JCPDS-ICDD files of standard minerals (about one month after cement and mortar delivery). Powder samples were studied as supplied, and as hydrated in water vapour, immediately after the termination of the respective water sorption/retention test (see below). Mortar samples were disintegrated by grinding in agate mortars.

Other tests done on these samples (thermo-XRD, IR/TG, MS, SEM) will be published separately.

Results and discussion

Mineral composition

Cement powder indicated the presence of alite, a, belite, b, brownmillerite, B and gypsum, G. The calcite basal spacing ranged between 3.036 and 3.041 Å, as increased by the presence of alite. In two mortars (CS-20-1m and CS-15-1m-WR3) the strong peak at 3.24 Å was found, belonging to microcline, M which was contained in the aggregate sand.

After hydration the peaks of portlandite, P, and ettringite, E, were observed; alite, a belite, b and brownmillerite, B were still present but in diminished amounts (peak intensity, Fig. 2a, CS-15-WR1). Calcite was forming, shown by the increase in the intensity of the joint calcite+alite peaks at 3.04 to 3.05 Å. Alite amount was small especially in mortars, as it transformed into portlandite, C–S–H gel and possibly other amorphous material. Its [009] peak at 2θ=32.1° was still present, in all the mortar samples, but the [–252] peak at 2θ=32.5° almost disappeared in case of t_g=20–25 min and in case of samples, hydrated subsequently in water vapour (WR1, WR2 and WR3).

The content of portlandite was the highest in mortars hydrated in liquid water (peak intensity, Fig. 2b, CS-30-1m). It was lower in powder samples (Fig. 2a) and in mortars after their subsequent hydration in water vapour: some part transformed into carbonates and the calcite peak intensity generally increased with time of storage in water vapour (WR1<WR2<WR3).

In all the hydrated samples there was an increased background between 2θ about 28 and 38°, revealing an amorphous material (mainly C–S–H gel at 2θ=32–36°, and possibly other components in amorphous or nanocrystalline form, e.g. CCH).

More detailed study showed the presence of peaks of CCH compounds (Table 6a) and of meta-stable carbonates (Table 7).

Table 3 Chemical and mineral composition of the clinker as measured in the plant laboratory by X-ray fluorescence analysis on molten sample (in mass%)

P.F.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	TiO_2	Mn_2O_3	Free Ca
0.15	20.95	4.05	4.71	66.97	1.03	1.55	0.42	0.17	–0.61	1.00

C_3S*	C_2S*	C_3A*	C_4AF*	gypsum	* Bogue method
70.87	6.70	2.78	14.31	3.5	

Table 4 Cement samples (plant data)

Grinding time/min	15	20	25	30
Sample	CS-15	CS-20	CS-25	CS-30
Specific surface/cm^2 g^{-1} Blaine	2.623	3.019	3.504	3.784
Compression strength/MPa	58.5±0.5	64.7±0.5	67.8±0.6	69.7±0.4

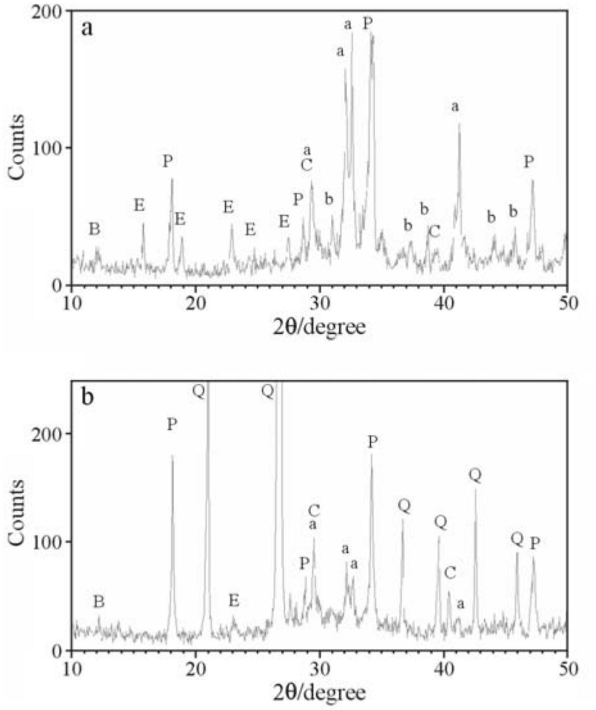

Fig. 2 XRD of a – CS-30-WR1 and b – CS-30-1m

Quartz contained in the aggregate sand indicated in mortars several peaks of the highest and variable intensity, thus they are presented out of scale to discern the smaller ones, Fig. 2b. This will be discussed in a separate publication.

Basal spacing of portlandite

The average values of basal spacing of portlandite, as registered in XRD in various diffractograms, were calculated and compared with the nominal ones, Table 5.

From the nine JCPDS-ICDD files of portlandite, the two were selected, which indicated the highest and the lowest basal spacing, and those representing the planes [001], [011] and [012] were subject to a farther analysis. The measured *d* values were contained between the lowest and the highest nominal ones. In the hydrated powder their variability was the biggest in case of *d*[011], it was small in case of *d*[001] and the smallest in case of *d*[012] (standard deviation, *sd*=0.005, 0.003 and 0.002, respectively, for *n*=12 samples).

The variation in *d*[001] was higher in mortars hydrated in liquid water (*sd*=0.003) than in cement powder, hydrated in water vapour (*sd*=0.006) but the average value itself was similar and also the remaining *d*[011] and *d*[012] showed almost no variability. Both the *d*[001] and its standard deviation increased after subsequent hydration in water vapour (WR, *sd*=0.009), but the variation of the other peaks was smaller.

Thus the CO_3^{2-} ions may enter the crystal lattice of portlandite, increasing its basal spacings, as they are bigger than the OH^- ions. Only the lowest standard value concerns the pure or almost pure $Ca(OH)_2$ [7].

XRD query of CCH compounds

It was not expected to get by XRD an unequivocal proof of the presence in hydrated cement of CCH compounds, of which 11 standard files were found, see Introduction. The system is multicomponent and complex, the amount of these compounds may be very small, their crystallinity poor and they may be present in amorphous form (e.g. CCH-1 and CCH-3 [9, 10]). The possibility of their existence may be though confirmed by analyzing their small individual XRD peaks and by checking the departure from symmetry of those coinciding. This possibility was strongly indicated by the IR spectroscopy [7].

All the peaks observed in the 32 diffractograms, including the smallest ones, were identified by computer and registered in eight tables (not presented here), referred to as A1 to A8 and these symbols will be applied to describe particular treatment: A1 represents dry cement powders CS-15 to CS-30, whereas A2, A3 and A4 – those hydrated subsequently at RH=1.0 (WR1, A2), at RH=0.95 (WR2, A3) and at RH=0.5 (WR3, A4). Similarly A5 corresponds to mortars CS-15-1m to CS-30-1m, hydrated in liquid water and A6, A7 and A8 – those hydrated subsequently at RH=1.0 (WR1, A6), at RH=0.95 (WR2, A7) and at RH=0.5 (WR3, A8).

All the peaks in the 8 tables were compared with crystalline cement components (a, b, B, G) and with the known products of cement hydration (P, E).

Table 5 Nominal and measured basal spacings of portlandite in Å

2θ	[*hkl*]	Nominal *d*[hkl]		After hydration		
		lowest*	highest**	Powder WR *n*=12	Mortar –1m *n*=4	Mortar,WR *n*=12
18.1	[001]	4.895	4.922	4.912±.003	4.910±.006	4.915±.009
34.1	[011]	2.622	2.627	2.625±.005	2.625±.001	2.627±.003
47.2	[012]	1.922	1.927	1.927±.002	1.926±.001	1.926±.002

*1-71-156, **44-1481

The unidentified peaks were compared with the characteristic values of CCH compounds (intensity, $I>10$), allowing for a possible influence of the coinciding ones, i.e. hydration products and unhydrated cement components of a similar basal spacing. The CCH compounds were assumed to be present if the peaks indicated a proper value or were properly displaced as compared with coinciding peaks, i.e. the measured $d[hkl]$ spacing of CCH was increased if the coinciding peak was higher, or decreased if the coinciding peak was lower. A certain difference between nominal and measured d-values was also acceptable in analogy with portlandite.

In case of unhydrated cement powder, most peaks of CCH were coinciding. After selection of the non-coinciding ones, the Table 6a was prepared and the number of $d[hkl]$ was found as 1, 3 and 2 in CCH-1, CCH-4 and CCH-5, encountered 2, 8 and 5 times, respectively. No CCH-2 and CCH-3 peaks were found. The number of peaks is supposed to represent the relative quantity of the given compound. Thus the carbonation reaction (1) was here in the advanced state.

Referring to the reaction (1a) it may be assumed, that this sequence of CCH compounds represents the sequence of carbonation reaction. The transformation of $Ca(OH)_2$ into $CaCO_3$ can be either gradual or stepwise with intermediate steps of the carbonate hydroxide hydrate character, and proceeds most probably as:

Portlandite (of increasing $d[hkl]$ spacings)$\rightarrow$calcium carbonate hydroxide (CCH-1)$\rightarrow$calcium carbonate hydroxide hydrate (CCH-2 and CCH-3)$\rightarrow$calcium carbonate-6-hydrate (CCH-4)$\rightarrow$monohydrocalcite (CCH-5)$\rightarrow$ calcium carbonate (1b)

The stoichiometry of CCH-2 is fractional and indicates rather to a continuous reaction. This may be a mixture though of compounds having the stoichiometry of integral numbers.

In the unhydrated cement powder the progress of carbonation reaction resulted in a high content of CCH-4 and a little less of CCH-5, whereas CCH-2 and CCH-3 were ‘used’ completely and CCH-1 was slightly ‘reproduced’.

The total number of non-coinciding peaks of CCH compounds in all the diffractograms of hydrated powder samples was 37, whereas in mortars it was 26. Also the amount of coinciding components (a, b, B) was here higher, as they hydrated less readily in water vapour than in liquid water. The total peak number decreased with grinding time down to t_{gr}=25 min (25 peaks at t_g=15 min, 16 peaks at t_g=20 min, 8 peaks at t_g=25 min) and then increased again to 14 peaks at t_g=30 min.

On hydration of cement powder in water vapour, the progress of carbonation reaction was similar as in the unhydrated powder (compare Table 6a with Tables 6b–c), but here all the CCH compounds were observed at a smaller amount of CCH-1 and CCH-2 (smaller number of respective peaks), whereas more CCH-3, CCH-4 and CCH-5 were found.

The result of mortar hydration was contrary (Table 6c): about twice more CCH-1 and CCH-2 peaks were found than those of CCH-3 to CCH-5. In the dense mortar structure the extent of carbonation reaction was much smaller.

When analyzing separately the various specimen of CCH, the increase in grinding time results in a decrease in number of CCH-1 to CCH-3 peaks (Table 6c), down to t_{gr}=25 min, increasing slightly at t_{gr}=30 min, which was not the case in CCH-4 and CCH-5.

The lowering of peak number with grinding time indicates that some groups sensitive to carbonation in the initial process are disturbed, but they are recovered at t_{gr}=30 min. This recovery is complete in CCH-3, partial in CCH-2 and CCH-4 and small in CCH-1 and CCH-5 (Table 6c).

The influence of hydration conditions is analyzed in Table 6d. The total number of peaks of ‘initial’ CCH compounds (CCH-1 and CCH-2) are less numerous in powder diffractograms. In case of the remaining compounds (CCH-3, -4 and -5) they predominate over those found in mortars, hydrated both in liquid water (1 m) and in water vapour. On hydration in liquid water (1 m) the extent of carbonation reaction is not important: the highest number of peaks was found for CCH-1, decreasing gradually down to

Table 6a Non-coinciding peaks of CCH compounds found in unhydrated cement powder (d in Å)

Compound	$d[hkl]$	d[exp]	Grinding time/min	No. of peaks
CCH-1	2.680	2.675	15 and 30	2
CCH-2	no			0
CCH-3	no			0
CCH-4	4.460 2.615 2.527	4.360–4.490 2.611–2.613 2.516	15, 25, 30 15–30 15	8
CCH-5	4.330 2.494	4.360–4.380 2.516	25–30 15	3

Table 6b Non-coinciding peaks of CCH compounds found in hydrated cement powder and in mortars (*d* in Å)

Compound	*d*[*hkl*]	*d*[exp]	Table	Grinding time/min	Total no.
CCH-1	2.940	2.944, 2.950, 2.927	A4, A5, A8	20, 15, 30	
	2.680	2.679, 2.682, 2.684	A5, A5, A8	15, 15, 20	11
	2.380	2.389, 2.355, 2.366	A2, A3, A3	15, 20, 25	
		2.383, 2.385	A5, A5	15, 20	
CCH-2	8.314	8.130, 8.549, 8.523	A3, A3, A5	15, 20, 30	10
	2.910	2.899, 2.885	A5, A5	15, 25	
		2.895, 2.894, 2.883	A7, A7, A8	15, 30, 15	2.877 b
		2.895, 2.894	A8, A8	20, 30	
CCH-3	8.570	8.549, 8.523	A3, A5	15, 30	14
	6.520	6.232, 6.598	A3, A4	30, 15	
		6.195, 6.395	A4, A4	20, 25	
		6.410, 6.488	A5, A5	15, 30	
	4.810	–			4.895 P
	3.610	3.610, 3.605	A2, A3	30, 20	
	2.112	2.131, 2.135	A2, A2	15, 25	
		2.132, 2.135	A4, A4	15, 30	
CCH-4	3.967, 3.983	3.997	A2	20	
	2.925	–			3.035 C + a
	2.687	2.677, 2.679, 2.682	A2, A5, A5	20, 15, 20	
		2.684	A8	15	13
	2.652	2.656, 2.652	A2, A2	20, 30	
	2.615	2.611	A4	15	
	2.527	2.522	A2	15	
	2.464, 2.479	2.476, 2.455, 2.461	A3, A3, A3	15, 20, 30	2.448 b
		2.455	A7	30	
CCH-5	4.330	4.313	A2	30	
	3.050	–			3.035 C + a
	2.494	2.522, 2.515	A2, A7	15, 15	2.560 Ett
	2.375	2.389, 2.374	A2, A2	15, 25	
		2.383, 2.385	A5, A5	15, 20	15
	2.159	2.159, 2.155	A2, A2	15, 25	
		2.155, 2.169	A3, A3	25, 30	2.165 b
		2.155, 2.163	A4, A4	20, 25	
		2.157	A8	15	
	1.939	1.935	A2	20	

Table 6c Number of XRD peaks of CCH compounds, found in hydrated powder and mortar and dependent on grinding time

Comp.	non-coinciding			in powder	in mortar	at t_{gr}/min 15	20	25	30
CCH-1	3	found	11x	4	7	5	4	1	1
CCH-2	2	found	10x	2	8	4	2	1	3
CCH-3	5	found	14x	11	3	5	2	2	5
CCH-4	6	found	13x	9	4	5	5	–	3
CCH-5	5	found	15x	11	4	6	3	4	2

CCH-5 (Table 6d). On subsequent hydration in water vapour the number of peaks rather decreased. The dense structure of mortar permits a limited penetration of carbon dioxide and only a small amount of CCH-1 and CCH-2 could have formed.

Interesting information may be obtained from the comparison of the peak numbers observed on hydration at RH=1.0 (WR1) both of the cement powders and mortars (Table 6e). In powder diffractograms this number increased gradually from CCH-1 (1) to CCH-5 (7), whereas in mortar diagrams it decreased in the same sequence, from 5 to 2. This indicates that the carbonation process is quicker in powder than in mortar. The variability at RH=0.95 (WR2, A3) was small, ranging between 2 (CCH-1, CCH-2 and CCH-5) and 3 (CCH-3 and CCH-4). At RH=0.5 (WR3, A4) the peak number of CCH-3 was exceptionally high (5), Table 6d.

Table 6d Influence of hydration conditions on the number of peaks encountered

Compound	Sample		WR1(A2)	WR2(A3)	WR3(A4)	
		1m(A5)	(A6)	(A7)	(A8)	Total
CCH–1	Powder		1	2	1	4
	Mortar	5	–	–	2	7
CCH–2	Powder			2		2
	Mortar	3		2	3	8
CCH–3	Powder		3	3	5	11
	Mortar	3				3
CCH–4	Powder		5	3	1	9
	Mortar	2		1	1	4
CCH–5	Powder		7	2	2	11
	Mortar	2		1	1	4

Table 6e Number of XRD peaks found after hydration at RH=1.0 (WR1)

Cement	CCH-1	CCH-2	CCH-3	CCH-4	CCH-5
Powder	1	–	3	5	7
Mortar	5	3	3	2	2

Table 7a Non-coinciding peaks of vaterite and aragonite found in hydrated cement powder and in mortars

Vaterite *d* measured/Å	*d*[*hkl*]/Å nominal	I	[*hkl*]	Table and (grinding time)/min
Vaterite [33-268]				
3.526-82	3.573	60	110	A1 (15 and 30), A2 (20), A5 (25)
2.103	2.113	20	008	A3 (25)
2.055-9	2.063	60	300	A2 (15 to 30), A3 (25), A4 (15 and 20), A5 (15 and 30)
Aragonite [41-1475]				
–	2.702	60	012	–
2.476-86	2.481	40	200	A3 (15), A5 (20)
2.366-84	2.373	45	112	A2 (25), A3 (25), A5 (15 and 20)
2.340-66	2.342	25	130	A3 (20 and 25), A5 (25)
–	2.108	20	122	–

Analysis for presence of vaterite and aragonite

Vaterite and aragonite are metastable polymorphs of calcium carbonate. Their nano-crystals and their XRD peaks were found previously mainly in powder hydrated in water vapour rather than in paste hydrated in liquid water [19] and their participation in the reaction chain is logical. They transform about 400°C into calcite and this reaction may proceed at lower temperature if sufficient time is allowed. In Table 7a some nominal basal spacings of these polymorphs of calcium carbonate are compared with the peaks observed in hydrated CS cements and mortars.

More vaterite than aragonite was forming in cement powder, especially if hydrated at RH=1 (WR1), Tables 7b and c, but in mortars their amount was similar (Table 7b). Vaterite formation was independent on grinding time, but aragonite content was increased by this parameter (Table 7b).

The hydration conditions of powder stored in water vapour were favourable for formation both of the CCH compounds and calcite polymorphs (Table 7d). On hydration of the mortar in liquid water the relative CCH peak number (N/n) was higher than that of hydrated powder, but on subsequent hydration of mortars in water vapour their relative number was much smaller; apparently their part was transformed to calcite (see below). In the previous study the intensity of carbonate peaks was smaller in hydrated paste than in powder [19].

More vaterite and aragonite peaks were observed on hydration in water vapour than in liquid water in mortars (vaterite prevailing), though the relative peak number was slightly lower in powder (Table 7d). On

Table 7b Number of XRD peaks of vaterite and aragonite, found in hydrated powder and mortar and dependent on grinding time

Comp.	non-coinciding		in powder	in mortar	at t_{gr}/min	15	20	25	30
Vaterite	3	found	11x	3x		4	3	4	3
Aragonite	3	found	5x	4x		2	3	4	–

Table 7c Influence of hydration conditions on the number of peaks encountered

Compound	sample	A1*	WR1(A2)	WR2(A3)	WR3(A4)	
		1m(A5)	(A6)	(A7)	(A8)	Total
Vaterite	Powder	2	5	2	2	11
	Mortar	3				3
Aragonite	Powder		1	4		5
	Mortar	4				4

*Dry cement powder

Table 7d Number (N) of non-coinciding CCH, vaterite (V) and aragonite (A) peaks, found in diffractograms of n samples (4 different grinding times, 3 water vapour conditions, WR1, WR2 and WR3. i.e. RH=1.0, 0.95 and 0.5, respectively); n=16 if unhydrated powder was included

Hydration conditions	No. of CCH peaks	Relative peak number: N/n	No. of V+A peaks (n=16)	No. of V peaks	No. of A peaks
Powder WR, n=12	N=37	3.08	23/16=1.44	11/16=0.69	5/16=0.31
Mortar (liquid water) n=4	N=15	3.75	7/4=1.75	3/4=0.75	4/4=1.00
and in WR n=12	N=11	0.92	–	–	–

the subsequent hydration of mortars in water vapour all their peaks disappeared, possibly transforming into calcite.

It is difficult to interpret the strongest peak of calcite (d[104]=3.035 Å), as it coincides with alite (d[0-41]=3.056 Å and d[–441]=3.041 Å) and it was observed in all the diffractograms under study. Its remaining peaks are much weaker (I<20) and generally slightly displaced. Some information may be derived from change in intensity of these peaks, which will be analyzed separately. The intensity of the strongest calcite peak increases on the subsequent hydration of mortars in water vapour, which would indicate the transformation of all the carbonates into this end product.

Conclusions

Unequivocal confirmation of the presence of the CCH compounds was not expected to be obtained from the XRD study of such a complex system, producing peaks of low intensity, frequently coinciding with other compounds and probably having amorphous form. It is important though, that their presence was not excluded and variation in their content was logical. The positive confirmation was obtained by IR/TG, presented elsewhere. From the found number of peaks some conclusions may be drawn, concerning the influence of particular hydration conditions.

- The presence of all the five CCH species was indicated by XRD in the hydrated cement CS (CCH-2 is least probable).
- Relatively more non-coinciding CCH peaks were found in mortars (15/4=3.75), than in hydrated powders (37/12=3.08), decreasing after subsequent hydration in WR (11/12=0.92; these ratios correspond to number of CCH peaks found, divided by the number of samples studied).
- In powder hydrated in water vapour the presence of CCH-1 and CCH-2 was less probable than that of CCH-3 to CCH-5, indicating an important progress of carbonation reaction.
- In mortars hydrated in liquid water the presence of CCH-1 and CCH-2 was more probable than that of CCH-3 to CCH-5, thus the carbonation reaction was here at the initial stage.
- Pre-grinding of cement (clinker) lowers the carbonation process down to grinding time t_{gr}=25 min. Most peaks were found after t_{gr}=15 min (25), less after t_{gr}=20 min (16), the least at t_{gr}=25 min (8) and slightly more at t_{gr}=30 min (14). This indicates that

grinding destroys some groups, reactive in carbonation, and reforms them at t_{gr}=30 min.

- After hydration at RH=1.0 (WR1) the peak numbers increased in powders in the sequence from CCH-1 to CCH-5 and decreased in the same sequence in mortars. This indicates that the gradual carbonation process is either quick, proceeding easier in the porous structure of cement powder, or it is slow due to a more dense structure of mortars.
- On subsequent hydration of mortar in water vapour the peak numbers either decreased (possibly dissolved or transformed into carbonates) or remained unchanged (CCH-3).
- More vaterite and aragonite peaks were found in hydrated powder than in mortar, though an opposite relation was true concerning their relative number. In a previous study (aged cement) the peak intensity was higher in powder, than in mortar.
- Vaterite formation was almost independent on grinding time, whereas that of aragonite increased with this process (except t_{gr}=30 min). More vaterite than aragonite was formed on cement powder hydration, whereas in mortar their content was similar. The metastable calcium carbonate polymorphs disappear on subsequent hydration in water vapour of mortar, as they transform into calcite.

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These results indicate that the suggested carbonation reaction is possible, geometrically as:

$$\underset{\text{hexagonal}}{\text{Portlandite}} \rightarrow \text{CCH-1} \rightarrow \underset{\text{orthorhombic}}{\text{CCH-2}} \rightarrow \text{CCH-3} \rightarrow \underset{\text{monoclinic}}{\text{CCH-4}} \rightarrow \underset{\text{hexagonal}}{\text{CCH-5}}$$

$$\underset{\text{hexagonal}}{\text{vaterite}} \rightarrow \underset{\text{orthorhombic}}{\text{aragonite}} \rightarrow \underset{\text{rhombohedral}}{\text{calcite}}$$

and chemically as:

Portlandite: $$2Ca(OH)_2+xCO_2\rightarrow 2Ca(OH)_{2-x}(CO_3)_{x/2}+xH_2O$$ *d*[001] increases

$$\underset{\text{portlandite}}{3Ca(OH)_2}+2CO_2\rightarrow \underset{\text{CCH-1}}{Ca_3(CO_3)_2(OH)_2}+2H_2O\rightarrow$$

$$\underset{\text{CCH-1}}{2Ca_3(CO_3)_2(OH)_2}+3H_2O\rightarrow \underset{\text{CCH-3}}{2Ca_3(CO_3)_2(OH)_2\cdot 1.5\,H_2O}$$

$$\underset{\text{CCH-3}}{2Ca_3(CO_3)_2(OH)_2\cdot 1.5H_2O}+31H_2O+2CO_2\rightarrow$$

$$\underset{\text{CCH-4}}{6CaCO_3(H_2O)_6}\rightarrow \underset{\text{CCH-5}}{6CaCO_3(H_2O)}+30H_2O\rightarrow \underset{V\rightarrow A\rightarrow C}{6CaCO_3}+36H_2O$$

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