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SIMULTANEOUS IR/TG STUDY OF CALCIUM CARBONATE IN TWO AGED CEMENT PASTES

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Two aged cement pastes (7 years) were studied for H_2O and CO_2 evolution, the combined amounts of which were measured by TG and identified by thermo-IR analysis. This indicated the presence of three forms of carbonates, which decomposed at different temperatures. The displacement with time of the evaporation of sorbed water to higher temperatures (500–700°C, TG, MS) shows the possibility of its incorporation into carbonate hydrates and/or hydroxy hydrates, postulated previously. The decomposition of all the hydration products needed a thermal energy increasing with ageing (increased temperature measured by TG). The carbonation process proceeded for 7 years in the weaker paste, whereas it terminated before 5 years in the stronger one. The CSH water content did not change with ageing, whereas that of portlandite was lowered, which though did not account for the increase in carbonate content (TG). Possibly some Ca^{2+} from the CSH gel was involved in this process. In the stronger paste the growth with time of organic matter was found (IR, TG/DTG).

Keywords: *calcium carbonate hydrates, calcium carbonate hydroxide hydrates, calcium carbonates, cement hydration and ageing, IR spectroscopy, TG/DTG/DTA, water in hydrated cement*

Introduction

Two cement pastes of different strength (C-33 and C-43) but of a similar chemical composition were tested previously by various methods after various ageing times to check the hydration and ageing products [1]. The simultaneous IR/TG study of H_2O and CO_2 evolution was done 2 years later (thus after total 7 years), to check the postulated transition between $Ca(OH)_2$ and $CaCO_3$ with some intermediate carbonate hydrates and hydroxide-hydrates [2].

Several species of these compounds are described in the JCPDS-ICDD files, such as ikaite [$CaCO_3{\cdot}6H_2O$], monohydrocalcite [$CaCO_3{\cdot}H_2O$], calcium carbonate hydroxide [$Ca_3(CO_3)_2(OH)_2$], calcium carbonate hydroxide hydrate [$Ca_3(CO_3)_2(OH)_2{\cdot}1.5H_2O$], defernite [$Ca_6(CO_{2.65})_2(OH_{.66})_7(H_2O)_2$], see [2]. Also some intermediate compounds are possible.

These problems are of importance: an ancient cement was found to contain mostly $CaCO_3$ [3]. Also it was shown that the tobermorite based materials indicate shrinkage on carbonation, which proceeds in the following way in the tobermorite 11 Å [4]: $5CaO{\cdot}6SiO_2{\cdot}5H_2O+5CO_2\rightarrow5CaCO_3+6SiO_2+5H_2O$

Materials and methods

Materials and methods were described in detail in previous publications, see [1]; they are presented here for the convenience of the reader.

Standard pastes were prepared of two Indian OPC cements of grade 33 and 43, supplied by NCB, New Delhi [IS: 8112-1989], of the chemical composition, Table 1. Their strength and also their specific surface were different, i.e. 146 and 166 $m^2\ g^{-1}$, respectively [1].

After the 28 days hydration at room temperature, they were air dried or pretreated with acetone and air dried (ac). Static heating [SH in triplicate] was done successively at 110, 220, 400, 600 and 800°C, expressing the mass loss, ΔM, in mass/mass% *vs.* the final mass at 800°C.

After 5 years ageing (unprotected from contact with air) the pastes were subject to

- thermal analysis, TG/DTG/DTA, at atmospheric pressure in air or in argon flow at 500 mL min^{-1}
- XRD on heating at 5 K min^{-1} registering the traces at the start of the peak, at the peak and its tail on the TG curve

Table 1 Chemical composition of the cements C-33 and C-43, in mass/mass% (NCB)

Cement	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	SO_3	Na_2O	LOI
C-33	61.8	24.4	5.6	3.0	1.8	0.77	2.2	0.25	2.3
C-43	61.0	20.9	5.3	3.1	3.6	0.89	1.5	0.45	2.7

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- IR spectroscopy in KBr disc at room temperature and after heating at 110, 220, 400 and 600°C
- MS – mass spectrometry of H_2O and CO_2 on heating up to 1000°C at 5 K min^{-1} in vacuum of $4\cdot10^{-5}$ mbar

The simultaneous IR/TG test was done after 2 more years (7 years ageing), on the paste sample disintegrated with a hammer and its mass was 20 mg. The TG balance Netzsch TG 209 (DTA/TG/DTG) was used, on heating in argon flow at 95 mL min^{-1} and identifying H_2O and CO_2 in the evolved gases by the IR spectrometer Bruker IFS66 with MCT detector, at the heating rate 15°C min^{-1}, within the heating range 26 to 950°C.

The respective values of T and ΔM were estimated graphically at intersection of approximately straight linear parts of the TG curve. The mass loss was interpreted as: sorbed water up to ~110°C, hydrate water ~110–220°C, CSH gel water ~220–400°C, portlandite water ~400–500°C, complex mass loss ~500–650°C and carbonate decomposition ~650–770°C.

Results and discussion

TG study

Mass loss on heating in air [1] of the fresh and of the 5 years old paste, is compared in Figs 1a and 1b, whereas Figs 1c and 1d present the 5 and 7 years old one, heated in argon (Table 2).

The content of sorbed water was lowered both in C-33 and in C-43, on ageing for 5 years. The carbonation in air proceeded both on ageing (*i*) and on heating (*ii*). (*i*) An increase in carbonate content on ageing was shown by a higher mass loss above ~700°C (Figs 1a and 1b). The carbonation process proceeded between 5 and 7 years in C-33, whereas it terminated in C-43 before 5 years (Figs 1c and 1d). (*ii*) After portlandite decomposition at ~500°C the sample mass increased due to carbonation on heating in air (Figs 1a and 1b), which did not occur in argon (Figs 1c and 1d).

The escape of either H_2O or CO_2 needed after ageing a higher thermal energy: the T of decomposition of particular components increased with time, Table 2, possibly due to growing of structural elements of CSH gel, i.e. tobermorite-like and/or jennite-like particles [5], which impeded the escape of evolved gases (compare clays).

In C-33 the sorbed water almost disappeared between 5 and 7 years, moving partly to water of hydrates (Table 2, column c). CSH gel water remained unchanged (column d), portlandite water (column e) decreased slightly, whereas both the mass losses at 520–650°C, column *f*, and those of carbonate decomposition 650–770°C, column *g*, increased pronouncedly. Thus an important carbonation and/or carbonate hydroxide hydrate development occurred and/or water molecules were chemically bound in some other way.

The exceptionally high mass loss between 200 and 479°C, observed in C-43 (column d) was due to the decomposition or escape of organic matter, which formed gradually on ageing (minimum at 348°C on the DTG curve, see also IR below). The decrease in portlandite water content (column e) was more important in C-43 than in C-33, though less CO_2 evolved from C-43 on carbonate decomposition (column g) and the total mass loss was similar after 5 and after 7 years ageing (Fig. 1).

Table 2 The hydration and ageing products estimated from the TG test result in argon/mass%

Paste argon	Value	Sorbed water and hydrates	CHS gel+ O.M.	Portland water	High T, Δm	CO_2 of carbonates	Residual Δm
a	b	c	d	e	f	g	h
C-33 5 years	T/°C Δm	–160 7.8	160–420 5.4	420–460 3.8	460–660 4.6	660–730 7.0	730–1000 1.3
C-33 7 years	T/°C Δm Peak/°C	110–220 1.2 4.9 157	220–464 5.5	464–524 3.3 490	524–653 5.4	653–713–773 4.5 9.3 751	773–870 1.4
C-43 5 years	T/°C Δm	–150 7.9	150–410 7.6	410–470 5.3	470–610 2.4	610–710 8.1	710–1000 2.0
C-43 7 years	T/°C Δm Peak/°C	120–200 1.3 5.0 154	200–300–479 3.5 8.6 348	479–506 2.9 492	506–625 2.8	625–675–742 1.3 5.7 710	844–930 1.0 1.6
Time		lower	no change	lower	higher	higher 33 lower 43	higher
C-33 *vs*. C-43		similar	lower (OM in 43)	5 years lower 7 years higher	higher	5 years lower 7 years higher	lower

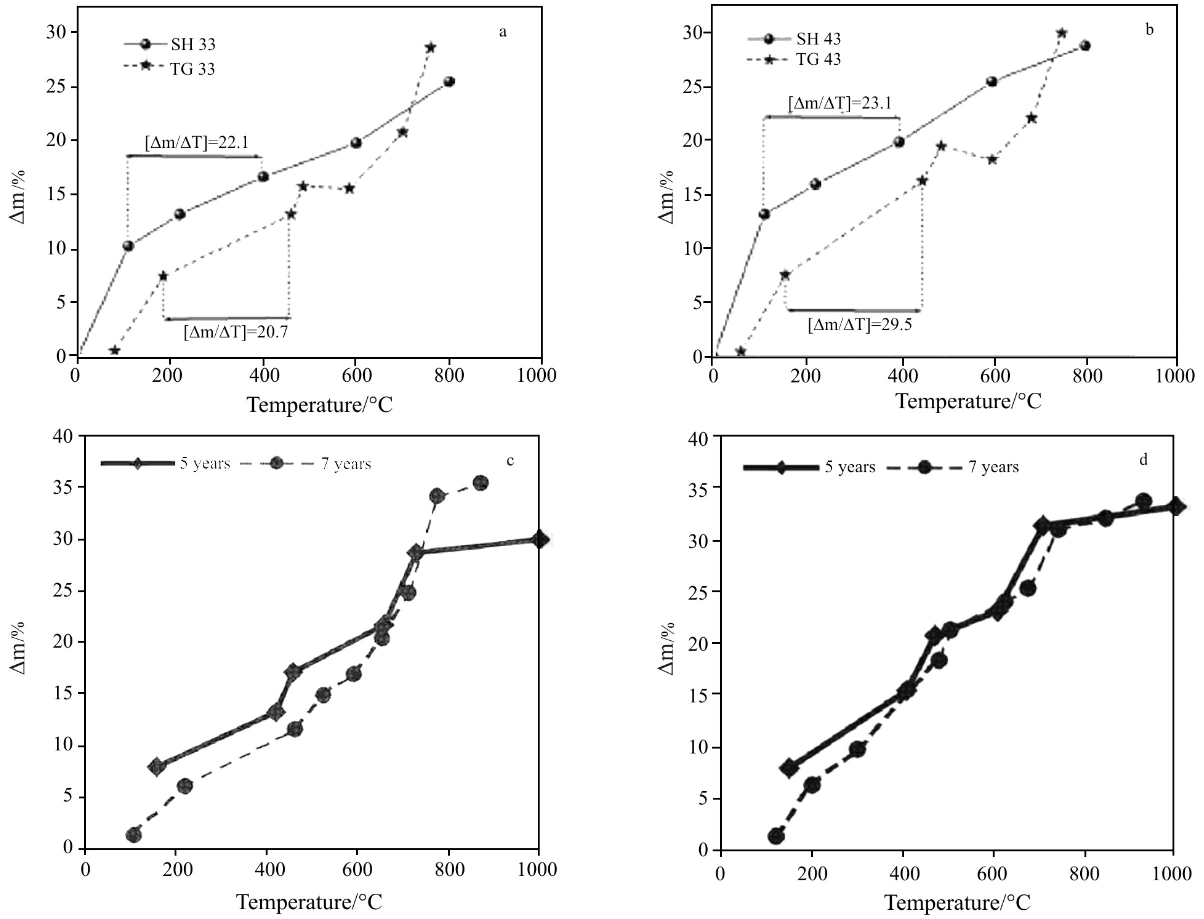

Fig. 1 Relation between Δm and T, of the freshly hydrated pastes (SH) and after 5 years ageing (TG), heated in air: a – C-33 and b – C-43; and after 5 and 7 years ageing (TG), heated in argon: c – C-33 and d – C-43

Thermo-IR spectroscopy

The total mass loss at the given T was measured in TG, whereas the H_2O and CO_2, evolving on heating from the hydrated cement pastes aged for 7 years, were identified by IR spectroscopy (Fig. 2).

The three regions of water absorbance (3500–3900, 1300–1800 and a broad band about 3229 cm^{-1}) correspond with those indicated by Farmer [6], as vibrations of gaseous water at 3656.65, 1594.78 and 3755.79 cm^{-1} (ν_1, ν_2, and ν_3, respectively).

Carbon dioxide vibrations of the linear molecule are reported at 1333 (symmetric stretching), 2349 (antisymmetric stretching) and 667 cm^{-1} (bending).

Organic matter was indicated by the three peaks between 2800 and 3000 cm^{-1}.

The IR spectra of the two cement pastes C-33 and C-43 were different (Figs 2a and 2b), the paste C-43 showing more features, which is presented below.

C-43

The peak values of water observed at about 370°C were: (*i*) within the first band 3904 (broad), 3736 (sharp) and 3587 to 3567 cm^{-1} (broad) and they existed at ~100–200°C (sorbed and hydrate water) at a small intensity and at an appreciable intensity about 500°C (portlandite water). The small peak ~3736 cm^{-1} remained up to 750°C. (*ii*) within the second band between 1300 and 1800 cm^{-1} the peak at ~1750 cm^{-1} was sharp and broad. The double peak at 1508 and 1458cm^{-1} was weak between 100 and 200°C and sharp ~500°C (portlandite water). At higher temperatures some noise is observable within this wave number range.

Carbon dioxide peaks in this cement paste C-43 were contained in two narrow bands: between 2361 and 2321 cm^{-1} and at 669 cm^{-1}, with additional peaks at 610 and 715 cm^{-1}.

CO_2 started to evolve above 200°C as indicated by the absorbance at ~2350 cm^{-1} and it became important above 300°C, escaping in three 'waves': between 200 and 450°C (maximum at about 350°C) between 450 and 700°C (the highest maximum at 630°C) and 700 to over 900°C (maximum at about 850°C, Fig. 2b). Thus the presence of three different species of carbonates is possible and this is in agree-

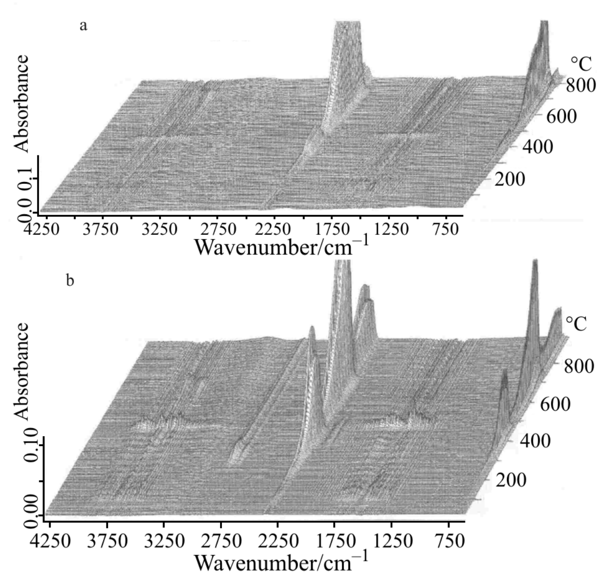

Fig. 2 IR spectra on heating in argon, of the pastes aged for 7 years: a – C-33 and b – C-43

ment with the MS observations, published elsewhere [1] and shown in Fig. 3.

The CO_2 absorbance peaks at 610–715 cm^{-1} occur at slightly higher temperatures, i.e. the first one between ~350 and ~500°C (maximum about 450°C), the second between ~500 and ~750°C (maximum about 650°C) and the third, broad between 750 and >900°C with the maximum possibly about 900°C. The peak at 669 cm^{-1} is very sharp and high above ~400°C and it is observable up to the highest T at lowering intensity. The peak about 650 cm^{-1} appears in the first and in the second range only, whereas at higher temperatures (>750°C) no vibration of this wave length was found.

All the CO_2–IR peaks *vs.* T are asymmetric (Fig. 2), tailing towards lower temperatures and dropping abruptly at the high T side and this is similar to the form of the DTG peaks [1]. The probable reason is the variable size of carbonate crystallites and/or a variable content of water and OH^- ions within the crystal lattice.

The triple peak of organic matter at 2926 cm^{-1} with its companions at 2958 and 2855 cm^{-1}, starts at ~300°C, increases to ~400°C and persists up to the highest temperature at low intensity, Fig. 4. This will be analyzed separately.

C-33

The spectrum of this paste is less differentiated and the respective peaks are smaller, except that of CO_2 at about 2300 cm^{-1} between ~500 and ~700°C (Fig. 2a). The wave numbers of the peaks are similar as in the paste C-43.

Water peaks are almost invisible between 100 and 200°C. Some peaks at ~3700 cm^{-1} are present both between ~450 and ~500°C and at higher temperatures, especially at 700 to 800°C. Their wave numbers at 670–700°C may be estimated as 3735 and 3705 cm^{-1}.

Carbon dioxide escapes also here in three 'waves', but the first one (350–450°C) and the third one (above 800°C) show a weak absorbance changing little with T. The peak between 500 and 700°C is important, with a maximum about 700°C (Fig. 2a).

Around the wave number 669 cm^{-1} the peaks in C-43 start at a more elevated T than in C-33, i.e. above 500°C. They form a shoulder at ~700°C, a peak at ~770°C and they drop at ~800°C.

No peaks of organic matter were found in this paste (Fig. 2).

Water

The amount of sorbed water measured at 110°C immediately after hydration, was 10.3 and 13.2% in C-33 and C-43, respectively, being proportional to the specific

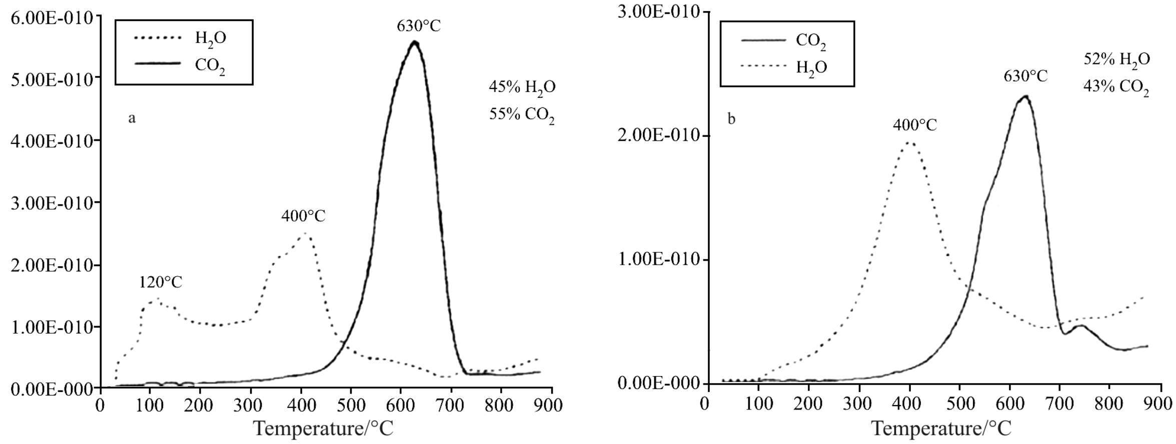

Fig. 3 MS in vacuum of the pastes a – C-33 and b – C-43, both aged for 5 years

surface, S=146 m^2 g^{-1} (C-33) or 166 m^2 g^{-1} (C-43). After 5 years it escaped up to 150–160°C amounting to 7.5 and 7.6%, respectively and after 7 years ageing it was only 1.2 and 1.3%, respectively (Table 2). The specific surface was lowered, i.e. the structural elements were bigger. The hydrate water could be identified after 7 years ageing (110–220°C) as 4.9 and 5.0% in C-33 and C-43, respectively.

The net O.M.+CSH gel water (~160–420°C after 5 years and ~200–480°C after 7 years) did not change importantly with ageing and it was in C-33: 6.4, 5.7 and 5.4% immediately after hydration, after 5 and 7 years, respectively. These values were higher in C-43 due to the growth of organic material which escaped about 350°C and which creates a separate problem.

Portlandite, $Ca(OH)_2$, was loosing water at ~410–470°C or at ~460–520°C in 5 and 7 years old pastes, respectively (compare XRD [7]), or in vacuum at 400°C (MS, Fig. 3, compare IR, Fig. 4), whereas the nominal value of $Ca(OH)_2$ decomposition is 580°C. The lowering of the decomposition temperature may be attributed to imperfections of the crystal lattice: a part of OH^- ions was substituted with time by CO_3^{2-} ions, derived from the carbon dioxide contained in air and this caused an increase in basal spacing of portlandite [7]. The nominal value of its $d(hkl)$ is 4.895 Å, whereas it was found in C-33 as 4.925 Å (after 1 year), and 4.936 Å (after 5 years). It was in C-43 : 4.916 Å and after wetting and drying: 4.927 Å both 1 year old. This shows also a lower sensitivity to carbonation of the stronger paste C-43 as compared to C-33 (see below).

Carbonates

The carbonation on ageing caused a slight decrease of the portlandite water content: in C-33 from 3.8 to 3.3% and a more important one in C-43 – from 5.3 to 2.9%, both between 5 and 7 years ageing. Such a decrease in portlandite water content in C-33 does not account for the high increase with time in mass loss at ~650–750°C (carbonate decomposition); moreover, it was inhomogeneous on prolonged ageing: 7.0% (5 years) and 4.5+9.3=14.8% (7 years) in C-33 and in C-43:8.1% (5 years) and 1.3+5.7=7.0% (7 years), Table 2, column g, as inferred from the curvature of the TG line. Thus either some other form of Ca^{2+} is involved, e.g. that belonging to the CSH gel, or some water, besides CO_2 escapes within this T range from the aged paste or both. The first reaction is more probable in C-33 as in this T range the water escape was negligible (Fig. 3a, MS). The second reaction is more probable in C-43, where the escape of water was found above 650°C (Fig. 3b).

Inhomogeneity is indicated also by the departure of the respective part of the TG curve from straight linearity. There are multiple small minima on the DTG curve. The carbonate minimum is seen at 710–750°C, but it starts actually right after the peak of portlandite decomposition, terminating abruptly on the high temperature side [1].

The lowered temperature of calcite decomposition is usually attributed to the small size of its crystallites contained within two ranges, i.e. micrite in chalk (1–4 μm), decomposing about 600°C and sparite of limestone (>10 μm), decomposing at about 630°C, whereas the monocrystalline calcite does it according to [8] at about 750°C.

In the hydrated and aged cement paste the size of crystallites would be expected to vary continuously, similarly as the T of their decomposition and indeed the IR peaks are tailing towards low T.

Both IR/TG tests (Fig. 2) and MS (Fig. 3) indicate though the presence of three types of carbonates which may evolve water. These types may be: (*i*) calcite decomposing at the highest temperature above 800°C (nominally at 898.6°C), (*ii*) calcium carbonate hydroxy hydrate and (*iii*) calcium carbonate hydrate, postulated previously [2]. Sorbed water, which evaporated from the fresh paste at low temperature, was most probably incorporated into the carbonate lattice on its formation, escaping between 500 and 700°C, Fig. 3 (and/or into the O.M., which is not discussed here).

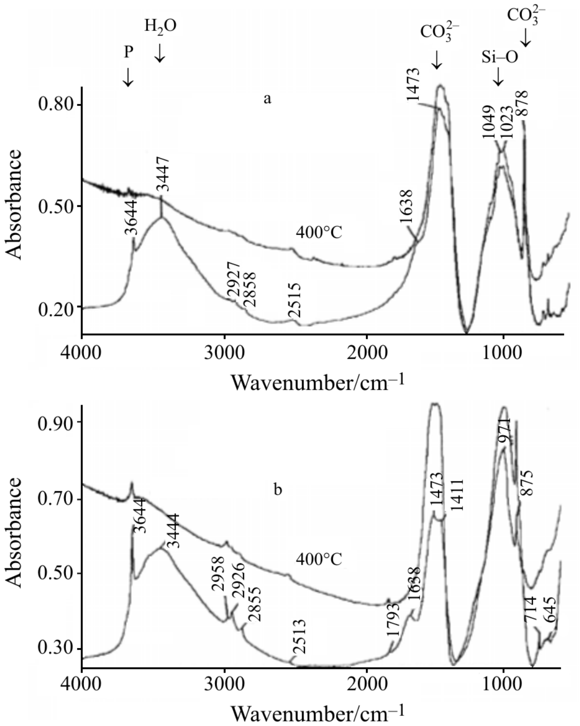

Fig. 4 IR spectra (in KBr) of the pastes a – C-33 and b – C-43, both pretreated with acetone, aged for 5 years, obtained either at room temperature, or heated at 400°C

Conclusions

The main hydration products considered here were in the sequence of increasing *T* of their decomposition: (*i*) sorbed water proportional to the specific surface, *S*, (*ii*) hydrate and CSH gel water occupying also the internal surfaces of tobermorite-like or jennite-like particles (in analogy with clays), (*iii*) portlandite, (*iv*) calcium carbonate hydrates and/or hydroxy hydrates, (*v*) calcite, formed on paste hydration, on ageing and/or on heating at 450°C from vaterite and aragonite (O.M. is only mentioned here).

Ageing causes an increase in the *T* of decomposition of all the hydration products, probably due to increase with time of the size of the structural elements (observed in clays), which impedes the escape of decomposition products.

The sorbed water is on ageing partly incorporated into compounds, decomposing at more elevated *T*, i.e. calcium carbonate hydrates and/or hydroxy hydrates (see above, (*iv*)) and/or O.M. Carbonation of $Ca(OH)_2$ [portlandite] and/or Ca^{2+} ions from CSH gel may also proceed, on reacting with CO_2 from air with formation of intermediate compounds (*iv*) which include these water molecules.

The weaker paste contained less water in all its forms, than the stronger one. More carbonates formed in the weaker paste, than in the stronger one, which contained an appreciable amount of all the three forms of calcium carbonate, found by IR and decomposing at different temperatures. In clay soils small amounts of carbonate may increase their strength, whereas its high amount may have a deteriorating effect. All the three calcium carbonate species (calcite, aragonite and vaterite) were found in hydrated and aged cement paste in form of nano crystals, which may have a strengthening effect.

A strong support was thus obtained to the postulated gradual formation of carbonates from calcium oxide and/or hydroxide with intermediate calcium carbonate hydrates and/or hydroxy hydrates.

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