HYDRATION PRODUCTS IN TWO AGED CEMENT PASTES

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The hydration products in two aged cement pastes (DTA/DTG/TG) were compared with those in fresh ones (static heating, SH) and were also studied by mass spectrometry (MS), IR and thermo XRD-analysis. The products considered here were: the sorbed water, the CSH gel including hydrates, portlandite, calcite, aragonite and vaterite. Except carbonates their content was higher in the stronger paste C-43, than in C-33, but lowered with ageing (only the CSH gel water remained approximately unchanged).

The sorbed water content became with time lower and similar in both pastes (it evaporated up to 155–185°C in TG); the escape of the rest moved to higher temperatures (500-700°C). The three DTG peaks at 200–400°C indicated jennite-like phase in the CSH gel; the mass loss (155–460°C) was higher on ageing due to development of organic matter, especially in C-43 (DTA, TG, IR). Portlandite content changed little and carbonate content increased considerably. They decomposed in air at 470 and 720–740°C, in argon at 450 and 680–710°C and in vacuum at 400 and 630°C, respectively (DTG peak, XRD). Between 500 and 700°C the simultaneous evolution of H_2O and CO_2 was observed by MS, which is attributed to dehydroxylation of jennite-like phase and/or to decomposition of some carbonate hydrate and/or hydrocarbonate (three peaks on CO_2 evolution curve, MS). The d(001) peak of portlandite exceeded the nominal value and will be analyzed separately.

Keywords: aragonite, calcite, cement hydration, C–S–H gel, DTA/DTG/TG, IR, mass spectrometry, mortar (paste) ageing, portlandite, vaterite, XRD

Introduction

Two ordinary Portland cements (OPC) of different strength were studied previously by various methods [1–2]. The mass loss on heating at temperatures, *T*, of these freshly hydrated pastes is compared here with that of the 5-year old one and the composition of the hydration products is checked by XRD, IR and mass spectrometry (MS). Thus its change with ageing is estimated. These changes as reported in the literature are presented below.

Hydration products in the freshly hydrated pastes

It is a general opinion, that in a hydrated ordinary Portland cement (OPC), containing initially alite and belite grains, the CSH gel forms the majority of solid volume and it is the primary strength giving phase [C→CaO; S→SiO_2; H→H_2O, thus CSH is $mCaO·nSiO_2·kH_2O$]. The other main hydration product is portlandite [$Ca(OH)_2$→CH] [3].

The CSH gel is related either to (I) tobermorite, $Ca_5(Si_6O_{18}H_2)·4H_2O$ [approx. $C_5S_6H_9$, CSH(I)], indicating a lower molar ratio $CaO/SiO_2<1.5$ or to (II) jennite, $Na_2Ca_8Si_5O_{30}H_{22}$ [$C_9S_6H_{11}$, CSH(II)], of disordered layer structure and of the above molar ratio equal to or higher than 1.5 [4–5]. At low Ca/Si ratios

[CSH (I)] a slightly higher binding energies are measured by X-ray photoelectron spectroscopy, due to a decreased Ca coordination and slightly shorter Ca–O bonds. The basic building block is SiO_4^{4-} and the negative charge is balanced by Ca-ion [6].

The initial reactions of OPC with water are connected with proton transfer and they are generally due to simple dissolution [7]; of importance are the physical factors, such as particle size distribution and microstructure [8]. The formation of CSH gel initiates from few nuclei and it grows to form branching 'ribbons' or bundles of lath-like particles of nano-crystalline regions [1–2]; this growth follows a kinetics mechanism of high order. Semi-ordered structure results, which is essentially amorphous as studied by XRD [9] or cryptocrystalline, composed of nanocrystals [2].

The CSH gel in young pastes consists mainly of dimeric silicate chains, linked by monomers to form pentamers as the hydration proceeds [10–12]. The CSH composition does not indicate systematic variation with age, whereas significant local inhomogeneities are observed. The microstructure is well established already after 24 h. Both microstructure and chemical composition are different in the inner and outer product, though the Ca:Si ratio is substantially the same, i.e. 1.7–1.8 [10, 13], but in a mature paste it may range between 0.8 and 2.1 [6, 9].

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

Cement	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	SO_3	Na_2O	LOI
C-33	61.8	21.4	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

Outer products form in the originally water-filled spaces, containing mainly fibrillar CSH gel, and $Ca(OH)_2$ [10] as massive crystals in large pores [1]. The spaces between the fibrils of CSH gel constitute the capillary porosity. A three-dimensional interconnected pore network is important for durability [10].

The inner product in a mature OPC paste consists most commonly of a single CSH phase of a compact homogeneous morphology inside the original alite/belite grains; it contains also unreacted material and may include all the major phases [AFm, AFt and $Ca(OH)_2$]; AFm has the general formula $[Ca_2(Al, Fe)(OH)_6] \cdot X \cdot xH_2O$ where X is usually OH^-, SO_4^{2-} and CO_3^{2-}, AFt is $[Ca_3 (Al, Fe)(OH)_6 \cdot 12H_2O]_2 \cdot X_3 \cdot xH_2O$ [3]. Portlandite is generally associated with the outer region [13]. This CSH phase in hardened OPC pastes is compositionally similar to that in alite and belite pastes only a small amount of Al is detected [10].

The pozzolanic reaction of CSH gel formation in the lime-pozzolan pastes proceeds in three phases controlled by: I. Pozzolanic reaction rate, II. Diffusion of reactants through a layer of porous hydration products, III. Diffusion of reactants through a layer of dense hydration products [14]. The raising of curing temperature accelerates the pozzolanic reaction rate [15].

Influence of ageing on the hydration products

The ancient cement mortars were studied extensively to assess the damage on ageing and on seismic activity and to prepare an adequate rehabilitation program, thus suitable testing methods are suggested [16].

Some Portland cement mortars after 600 days ageing contained in the outer CSH gel the crystalline CSH, portlandite, ettringite and a phase, similar to monosulfate [17]. Sulphation processes occur on surfaces of ancient and recent hydraulic mortars leading to gypsum formation on their exterior [18].

Polymineral cement grains were substantially preserved in the hydrated material of a 23-year old Portland cement paste [19]. In the outer product, the migration of ions was observed by TEM in a paste several years old and was dependent on ionic size [2].

In ancient-to-modern Cretan mortars the portlandite was found to be almost completely transformed into calcite contained in the matrix [20]. In the historic Venetian masonry, a completely carbonated lime existed in form of white lumps [21]. Similar lumps were present in the aged pastes stored in water vapour [1].

In the traditional pozzolanic mortars (Rhodes, Greece, Hagia Sophia) the CSH binding phase was found and it was similar to that encountered in the OPC as formed from slaked lime and fine reactive siliceous source at a temperature below 100°C. The pozzolanic reaction rate was limited by the dissolution of the siliceous source in the saturated $Ca(OH)_2$ solution [22].

In young pastes the CSH gel composition varied between the inner and outer product, but in pastes some years old a single composition predominated [19, 23].

Materials and methods

Two OPCs from India of grade 33 and 43 were supplied by NBC, New Delhi, in form of standard cubes of the paste at w/c=0.4. Hydration time was 1 month at r.t. After either air drying or acetone treatment [ac] and air drying, they were studied by static heating (SH), presented elsewhere, jointly with the results of XRD, SEM and HRTEM of the pastes about 1 year old [1, 24]. The chemical composition of both pastes was similar (Table 1) but they differed in strength, and in specific surface, which in the hydrated state was 146 and 166 $m^2 g^{-1}$ in C-33 and C-43, respectively [24].

After ageing for about 5–6 years, unprotected from contact with air, these pastes were studied by the following methods:

- TG, DTG and DTA, at atmospheric pressure, either in air or in argon atmosphere (A) at a gas flow of 500 $cm^3 min^{-1}$ (Seiko TG/DTA 6300, 1 K min^{-1}, up to 1000°C). The exact values of ΔM and T were found graphically as the intersections of tangents to the TG curve and calculated in mass percent *vs.* the final mass after heating.
- Mass spectrometry (MS) of H_2O and CO_2 (Balzers Quadstar quadrupole QMS200 mass spectrometer, heating rate 5 K min^{-1}, vacuum 4×10^{-5} mbar)
- IR spectroscopy in KBr disc, at room temperature and after heating at 110, 220, 400 and 600°C, 24 h in each case (NICOLETTE, FTIR 510)
- XRD (Philips X-pert, with a high temperature chamber ANTON PARR, HTK 1200, X'celerator, copper tube and θ–θ goniometer) at temperatures corresponding to the peak on the DTA/DTG curve, to peak's start and to its tail. The heating rate was 5 K min^{-1} and the goniometer rate was 5.4° min^{-1} for a total time 12 min 18 s for the 2θ range 5 to 65°and detector range 2.118°
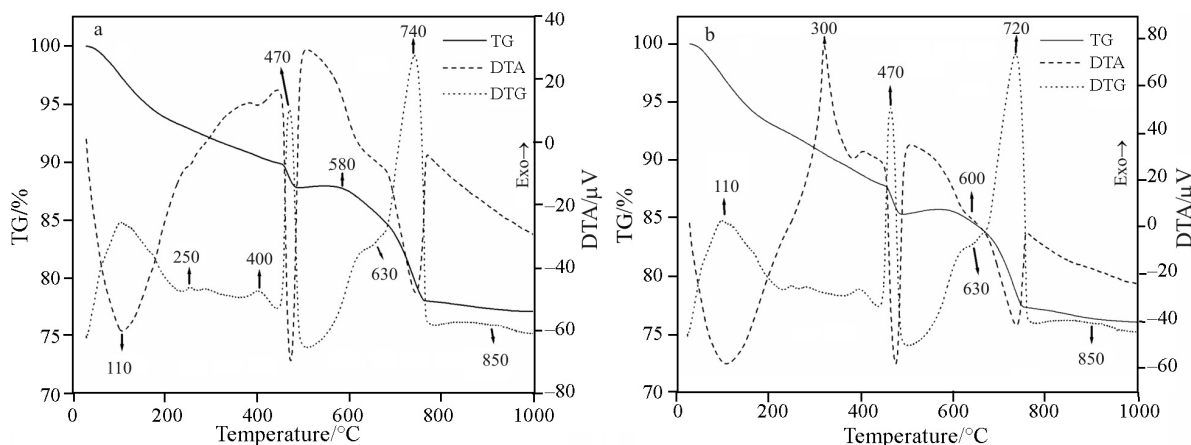
Fig. 1 DTA, TG and DTG curves of the aged paste C-33 (a) and C-43 (b), both heated in air atmosphere

Results and discussion

Thermal analysis

DTA/DTG test results

Thermal effects were observed at similar temperatures in both aged pastes (Figs 1a and b).

A peak at 110–120°C of the physically sorbed water and 2–3 peaks between 200 and 400°C of the dehydration of the CSH gel (at 250, 290–300 and 385–400°C) were found. The strong exothermic effect at 300°C (DTA curve of the paste C-43, Fig. 1b), much weaker in C-33 (Fig. 1a) was due to organic matter (O.M.) decomposition, connected with a strong heat evolution, which was not seen on heating in argon atmosphere (see below, MS).

Dehydration of portlandite [$Ca(OH)_2$] occurred at 470°C in air and at 450°C in A. Between 500 and 700°C the following was observed: (i) the carbonation of $Ca(OH)_2$ in air: between 500 and 600°C the mass increased (ΔM decreased, Fig. 1, Table 2), which was not found in A (see below MS and Table 2), (ii) the possible dehydroxylation at 630-660°C of the phase formed from CSH gel (an inflexion on the DTA/DTG curve at 630°C), (iii) the possible dehydration and decomposition of some carbonate hydrate and/or hydro-carbonate. Simultaneous H_2O and CO_2 escape occurred within this temperature range (see below, MS). All these effects were better observed in the stronger paste C-43 than in C-33 (Fig. 2). Carbonate decomposition occurred in air at 720–740°C and in argon at 680–710°C.

The temperature ranges of respective effects (TG/DTG) were in approximate agreement with those assumed in the static heating interpretation of the fresh pastes [1].

The influence of ageing on mass loss by heating

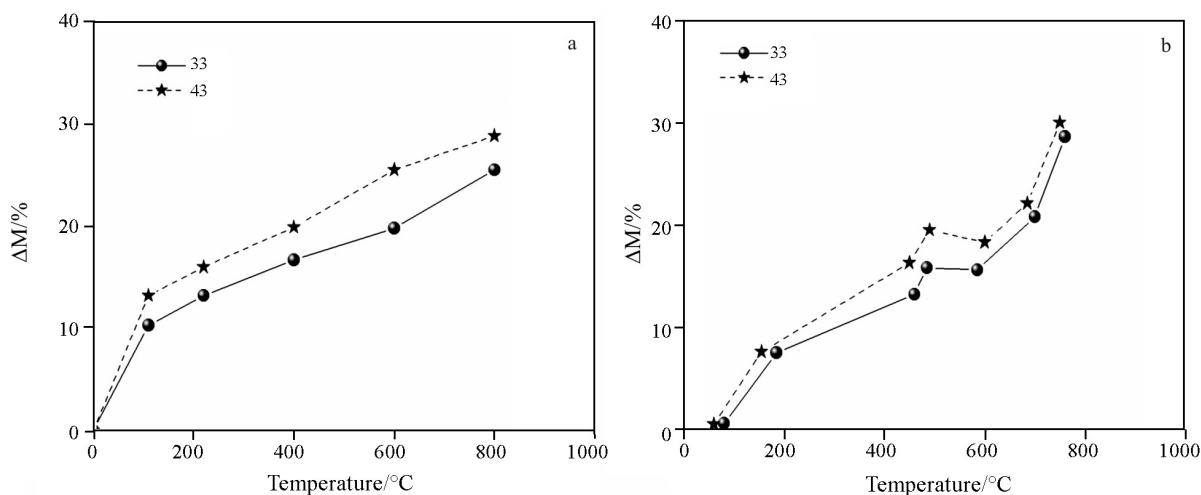Ageing caused a decrease in almost all the values of mass loss both in C-33 and in C-43 (Figs 3a and 3b,

Fig. 2 The influence of the paste quality on the mass loss on heating in air of the freshly hydrated pastes (a, SH) and of the aged ones (b, TG)

Table 2 Change with ageing in the content of hydration products in two cements [mass/mass %]

Paste	Test		sorbed water	CSH gel &hydrates	portlandite water	high T ΔM	CO_2 of carbonates	residual	$\Delta M<0$
a	b	c	d	e	f	g	h	i	j
Fresh	SH air								
C-33		$T/^{o}C$	110	110–400	400–600	–	600–800		
		ΔM	10.3	6.4	3.1		5.7		
C-43		$T/^{o}C$	110	110–400	400–600		600–800		
		ΔM	13.2	6.7	5.6		3.3		
Aged	TG air								
C-33		$T/^{o}C$	185	185–460	460–485	485–700	700–760	to 1000	485–585
		ΔM	7.5	5.7	2.6	5.2	7.8	1.3	−0.2
C-43		$T/^{o}C$	155	155–450	450–490	490–685	685–750	to 1000	490–600
		ΔM	7.6	8.7	3.2	2.6	7.9	1.8	−1.2
Aged	TG argon								
C-33		$T/^{o}C$	160	160–420	420–460	460–660	660–730	to 1000	
		ΔM	7.8	5.4	3.8	4.6	7.0	1.3	
C-43		$T/^{o}C$	150	150–410	410–470	470–610	610–710	to 1000	
		ΔM	7.9	7.6	5.3	2.4	8.1	2.0	
Aged	TG air								
C-33 ac		$T/^{o}C$	185	185–460	460–490	490–680	680–750	to 1000	
		ΔM	8.3%	5.9%	3.1%	4.3	7.7	1.1	
C-43 ac		$T/^{o}C$	160	160–460	460–480	480–710	710–740	to 1000	480–530
		ΔM	8.0%	7.7	2.3	11.1	6.8	2.2	−0.9

respectively), except ΔM(500–700°C) and ΔM (700–800°C) due to CO_2 escape, which was more dominant in aged pastes, as with time there occurred a pronounced carbonation of $Ca(OH)_2$.

The content of physically bound, sorbed, water, (TG straight line up to 150–185°C) decreased with ageing from 10.3 and 13.2% to 7.5 and 7.6% in C-33 and C-43, respectively.

The escape of hydrate water with CSH dehydration was indicated by a straight linear section of the TG-curve up to 460°C (starting from 155–185°C, corresponding to 110–400°C in SH). This value was by 0.7% smaller in aged C-33 than in the fresh one (Table 2, column e) whereas it increased by 2% after ageing of the paste C-43, partly due to decomposition of some organic matter, which developed on ageing (see DTA curves in Fig. 1). This decomposition resulted in mass loss ΔM=0.3% and 1.1% in C-33 and in C-43, respectively (difference in ΔM measured in air and in argon). Thus the 2% difference in this value between the fresh and aged paste C-43 may be due both to combustion of O.M. and dehydration of CSH gel in about equal parts.

This is also reflected in the value of the derivative $\Delta M/\Delta T$, which is similar in SH of C-33 and C-43 (22.1 and 23.1), but is slightly lower in TG of C-33 and higher of C-43 (20.7 and 29.5, respectively), Fig. 3.

The water content of portlandite changed little with ageing as it was similar in fresh paste (3.1 and 5.6%) and in the aged ones measured by TG in argon (3.8 and 5.3% in C-33 and C-43, respectively, Table 2, column f). The lower values measured in air (2.6 and 3.2%) are due to a partial carbonation of $Ca(OH)_2$ by the reaction with CO_2, which may proceed at 500 to 600°C after portlandite decomposition at 470°C (Fig. 1), resulting in an increase in mass (0.2% in C-33 and 1.2% in C-43, Table 2, column j).

All the carbonates decomposed above 700°C and the sensitivity to carbonation, which in the fresh pastes was ΔM(600–800°C)=5.7% (C-33) and 3.3% (C-43), increased with ageing in both pastes to ΔM(685–760°C)=7.8–7.9% (thus almost identical, Table 2, column h), in agreement with literature data on ancient mortars [20, 21].

The last section of the TG curve (800–1000°C), not measured in SH, corresponds to crystallization of the amorphous, anhydrous material of CSH gel, principally to belite, C_2S, alite, C_3S, and possibly wollastonite $CaSiO_3$ [5], ΔM amounting to 1.3–1.8% in air, 1.3–2.0% in argon and 1.1–2.2% after acetone pretreatment (Table 2, column i).
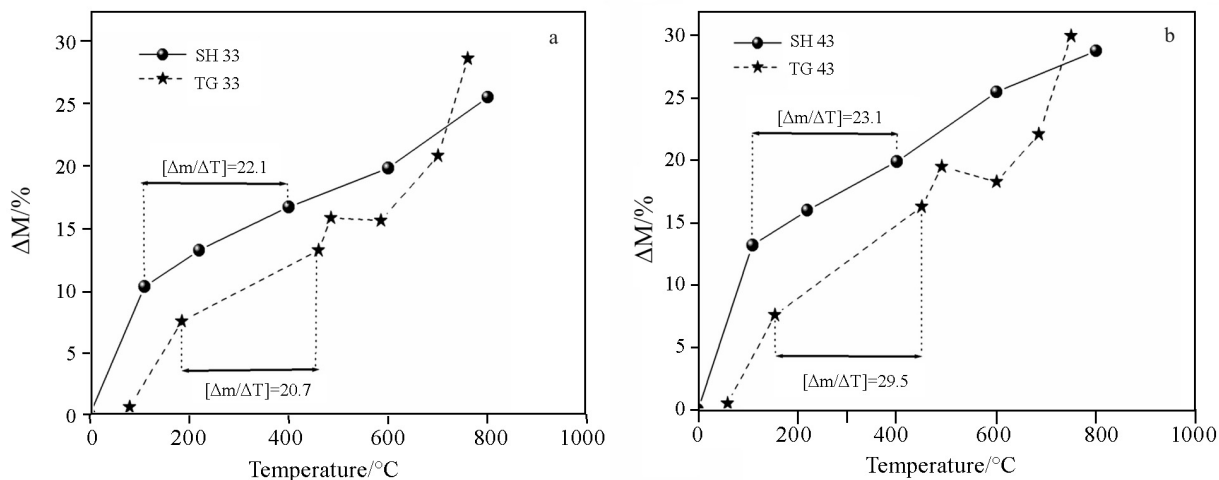
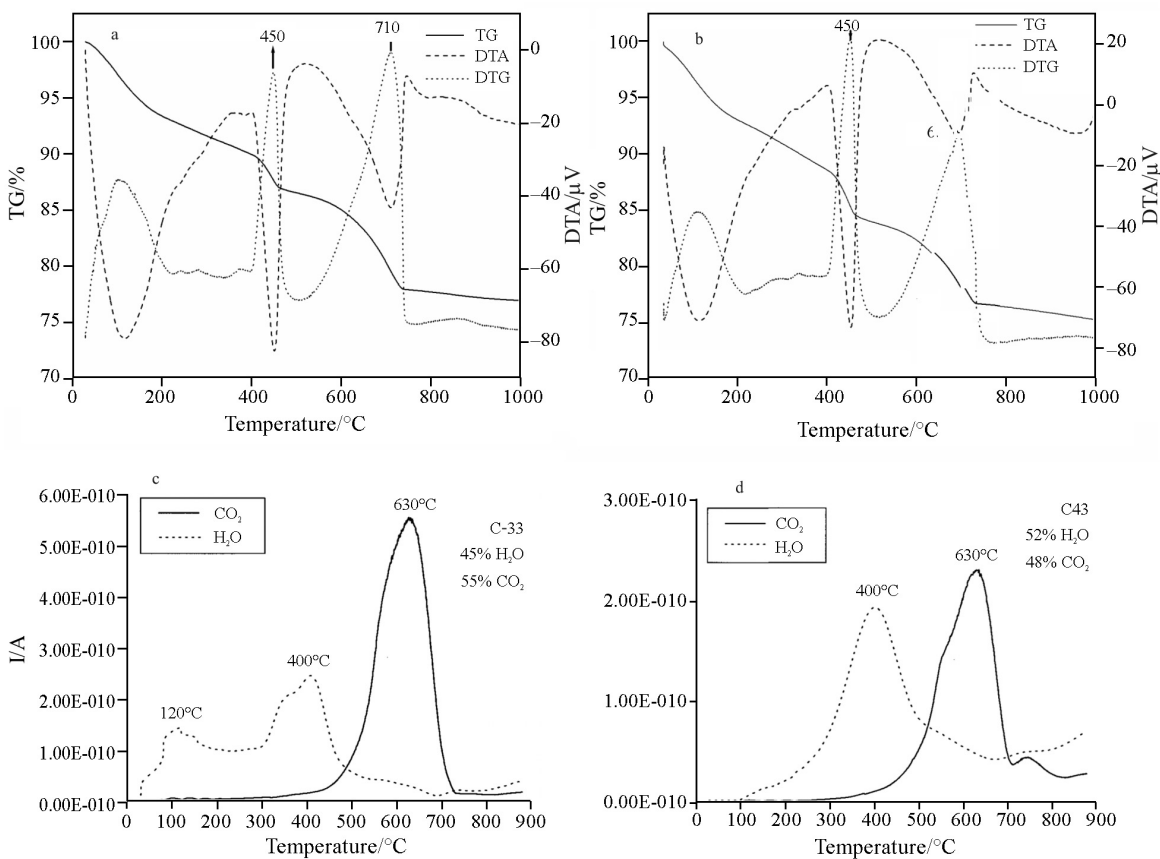**Fig. 3** The influence of ageing on the mass loss on heating in air of the paste C-33 (a) and C-43 (b)

Fig. 4 DTA, TG and DTG curves of aged paste C-33(a) and C-43 (b), both heated in argon atmosphere. Mass spectrometry of the aged paste C-33 (c) and C-43 (d), both heated in vacuum

The total mass loss up to 1000°C, was in aged paste C-33 somewhat influenced by the measuring conditions and sample pretreatment (29.9–30.4%). These values were much higher in C-43, i.e. 31.8% in air, 33.3% in argon and 38.1% after acetone pretreatment.

The influence of the heating atmosphere and of pretreatment

The mass loss on heating of aged pastes was measured by TG either in air [*a*] or in argon [A] and they were either air dried or pretreated with acetone [ac] before air-drying. Some differences were ob-

Table 3 Peaks (cm^{-1}) on the FTIR curve (C – calcite, A – aragonite, V – vaterite, O.M. – organic matter)

C-33-ac	C-43-ac
3674 cm^{-1}: increases with T; O–H stretch in hexagonal hydrates	3690 cm^{-1}: at 220°C, O–H inner surface
3644 cm^{-1}: O–H in portlandite, up to 400°C	3644 cm^{-1}: O–H in portlandite, lower at 400°C disappears at 600°C
	3526 cm^{-1}: at 110°C; O–H in hexag. hydrates
3447 cm^{-1}: decrease with T, OH stretch. H$_2$O	3444 cm^{-1}: at 30°C>, O–H stretch. in H$_2$O
2966 cm^{-1}: O.M.	2958 cm^{-1}: O.M.; at 30°C > at 400°C
2927 cm^{-1}: O.M. and CO$_3$$^{2-}$	2926 cm^{-1}: O.M.; disappears at 600°C
2858 cm^{-1}: O.M.	2855 cm^{-1}: O.M.
2515 cm^{-1}: calcite; no change with *T*	2513 cm^{-1}: calcite, increase to 600°C
2364 – 2346 – 2343 cm^{-1} adsorbed H$_2$O/CO$_2$?	
2198 cm^{-1}: at 600°C?	
1829 cm^{-1}: Magnesite, increase at 600°C	1793 cm^{-1}: calcite incr. 400°C, lower 600°C
1638 cm^{-1}: H$_2$O deform. ; only at 30°C	1638 cm^{-1}: H$_2$O ν_2 ; only at 30°C
1488 cm^{-1}: A + V	
1473 cm^{-1}: A + V	1473 cm^{-1}: A+V, decrease to 400°C, no at 600
1449 cm^{-1}: A + V + C	
1417 cm^{-1}: C, up to 600°C, in CSH	1411 cm^{-1}: calcite CO$_3$$^{2-}$ ν_{3},, increase to 600°C
1121 cm^{-1}: Si–O stretch.	
1070 cm^{-1}: Si–O, jennite [31]	
1048 cm^{-1}: Si–O, stretch. longitudinal	
1023 cm^{-1}: Si–O, stretch.	
971 cm^{-1}: Si–O in CSH, ν_3, SiO$_4$	971 cm^{-1}: Si–O in CSH; whole T range
876 cm^{-1}: C + V	875 cm^{-1}: C+V; increase at 400°C
745 cm^{-1}: C + V	
713 cm^{-1}: C + A	714 cm^{-1}: C + A
671 cm^{-1}: gypsum?	645 cm^{-1}: Al–O or C–A–H
537 cm^{-1}: Al–O–Al, tobermorite	521 cm^{-1}: C$_3$S, C$_2$S; at 400 & 600°C
486 cm^{-1}: Si–O–Si, tobermorite	464 cm^{-1}: C$_3$S, tobermorite, up to 220°C?
443 cm^{-1}: Al–O in CAH, tobermorite	

served between the ΔM values, and between the *T* ranges (Table 2).

In argon the *T* ranges of the thermal effects were lower than in air and generally the mass losses were higher. There were three exceptions: (i) the mass loss between 150 and 460°C was higher in air due to combustion of organic matter, which did not proceed in argon (see below, IR), similarly as (ii) the mass loss between 500 and 700°C and (iii) CO$_2$ escape from C-33.

Acetone pretreatment also altered the mass loss on heating in air and the temperature range of these effects was different in C-33 and C-43 (lowered for sorbed water content in C-43 and for CO$_2$ escape in C-33).

Mass spectrometry (MS)

The evolution of H$_2$O and CO$_2$ on heating was measured by the MS test in vacuum. The decomposition

of particular compounds occurred at a lower temperature, than at atmospheric pressure either in A or in air (DTG, Figs 4 and 1). Portlandite decomposed in vacuum at 400°C (Figs 4c and 4d), as compared to 450°C in A (Figs 4a and 4b) and 470°C in air (Fig. 1). Similarly the calcite main peak occurred at 630°C in vacuum (MS, with a secondary small effect at 750°C), as compared to 710–680°C in A (Fig. 4) and 740–720°C in air (Fig. 1).

The two pastes behaved in MS below 400°C quite differently: escape of sorbed water caused a peak at 120°C in C-33, not seen in C-43. Some effect took place about 350°C, before portlandite decomposition of a symmetric peak at 400°C. Corresponding DTG peaks at 240, 280 and 380°C in C-33 (Fig. 4a), were due to dehydration of jennite-like phase in CSH gel [5], and were smaller in C-43 (Fig. 4b). The peak symmetry was lost about 500°C, where the H$_2$O and

Table 4 Most important XRD reflexions observed in the aged pastes C-33 and C-43

Component	d/Å	2θ	h k l	d/Å	2θ	h k l	d/Å	2θ	h k l
Portlandite	4.94–4.92	18.0°	0 0 1	3.11	28.7°	1 0 0	2.63	34.1°	1 0 1
Calcite	3.04	29.4°	1 0 4	2.29–2.28	39.4°	1 1 3	2.10	43.0°	2 0 2
Aragonite	3.40–3.41	26.2°	1 1 1	2.10	43.0°	1 2 2	1.98	45.8°	2 2 1
Vaterite	3.58–3.57	24.9°	1 1 0	3.30–3.29	27.0°	1 1 2	2.74	32.6°	1 1 4
Alite&belite	2.78	32.2°		2.74	32.6°				
CaO[630°C]	2.43	37.0°	1 0 4						

CO_2 lines intersect, above which the slope of the H_2O line was less steep, and the further water escape was possibly due to formation of CaO, belite, alite and wollastonite (XRD, [5]). In C-43 only a symmetric peak at 400°C was found.

CO_2 evolution started at about 300°C and about 500°C the curve intersected with that of H_2O, thus the loss of both compounds was similar. A bump on the CO_2 curve at about 550°C and the asymmetric shape of the peak indicate some thermal effect at this temperature. The most important peak was found at 630°C, before a final drop to about 700°C, followed by a small peak about 750°C in C-43.

The thermal effects at 550°C, 630°C and 750°C indicate the presence of three compounds, decomposing with CO_2 evolution and accompanied by some loss of water. The thermal effects of water escape were observed at 120, 350, 400 and 500–650°C (carbonate hydrates and/or hydrocarbonates) and above 700°C.

IR spectroscopy

The absorption bands at wave numbers characteristic of all the compounds discussed above, were found in the IR spectra of pastes C-33-ac and C-43-ac (Figs 5a and b and Table 3, compare [27]).

Considerable amount of portlandite (3644 cm^{-1}) was present in both pastes, at a lower absorbance in C-33, disappearing at 400°C, and a higher one in C-43, decreasing at 400°C and disappearing at 600°C. In C-43 its peak exceeded the water peak at 3447-3444 cm^{-1}. This water peak was also relatively higher in C-43 than in C-33 and it decreased with temperature, disappearing at 220°C.

The content of carbonates in C-33 exceeded that in C-43 (absorbance band between 1488 and 1411 cm^{-1} and the peaks at 1793, 875 and 714 cm^{-1}) and the values of the wave number were somewhat higher in C-33, due to its more elevated content of vaterite and aragonite, which wave numbers exceed those of calcite : C-33: 1488, 1473, 1449, 1417 cm^{-1} and C-43: 1473, 1411 cm^{-1}. On heating the peaks moved to lower values, due to transformation at about 400°C of the metastable compounds (vaterite and aragonite) to calcite of the wave numbers 1450–1420 cm^{-1}, 1493–1470 cm^{-1} and 1435–1410 cm^{-1}, respectively [25–26]. This last compound is prevailing in C-43.

The contents of the Si–O compounds was higher in C-43 than in C-33 : the silicate absorbance band at 971 cm^{-1} was similar (C-43) or lower (C-33) than that of carbonate about 1470 cm^{-1} and at 400°C.

Three peaks at 2958–2960, 2926 and 2855 cm^{-1} in both pastes indicate the organic matter, which proceeded either from acetone pretreatment (C-33), or was accumulated in a higher amount during ageing (C-43, compare TG), but disappeared about 400°C.

X-ray diffraction at varying temperature

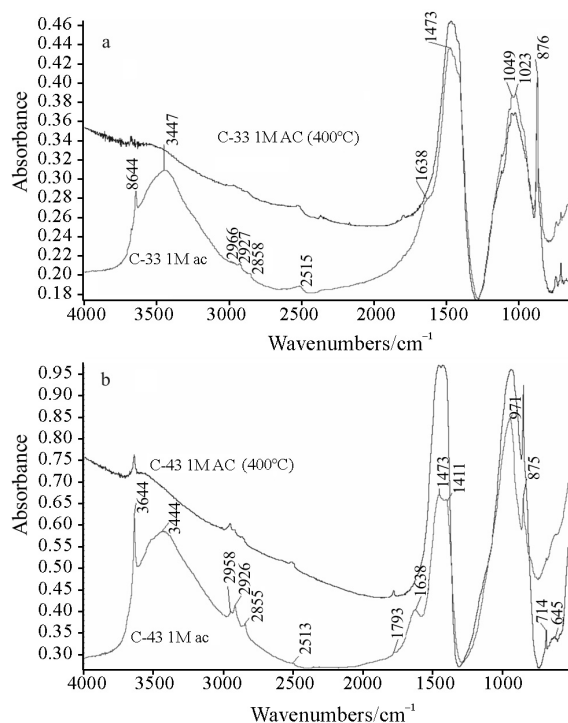At room temperature the portlandite peak in both pastes was of highest intensity as compared to the re-

Fig. 5 IR spectra recorded at room temperature and after heating at 400°C of the aged paste C-33 (a) and C-43 (b), both pretreated with acetone
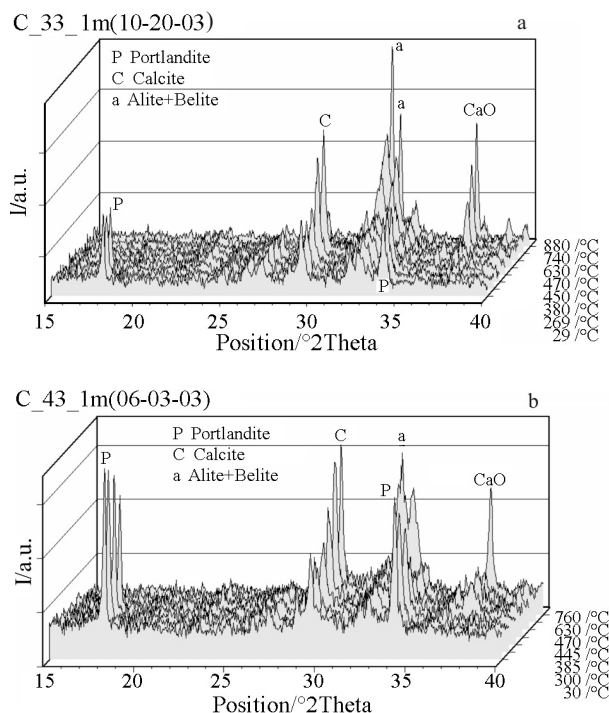
Fig. 6 XRD patterns of aged pastes at elevated temperatures as indicated: C-33 (a) and C-43 (b)

maining compounds (Fig. 6). The *d*(*hkl*) spacings exceeded the nominal ones (Table 4), which is discussed separately [27, 28]. All the three polymorphs of CaCO$_3$ were present (calcite, vaterite and aragonite). The relative intensity of the carbonate peaks was higher in C-33 than in C-43 (compare IR).

Some unhydrated *alite* and *belite* were observed (slightly more abundant in C-33 than in C-43) and their main peaks were sticking in the background band of amorphous CSH gel between 32 and 33°, (2.80–2.71 Å).

The X-ray diffractograms of C-33 and C-43, obtained at various *T* are discussed in detail in [28]. The highest peak of portlandite at 4.9 Å, decreased on heating at 400–450°C and disappeared at 470°C (compare DTG, Fig. 1). The highest calcite peak at 3.04 Å was in C-43 at room *T* low and broad, whereas in C-33 it was similar to that of portlandite. Its intensity did not change up to about 400°C, above which it increased gradually up to 600°C, decreasing gradually and disappearing at 740°C.

Alite and belite peaks, did not change up to about 500–600°C above which they started to increase up to the final *T*=760 or 880°C. At 630°C the CaO peaks appeared and they increased also up to the final *T*=880°C. At 630°C and above, the Al$_2$O$_3$ was observable in C-43, which occurred also in C-33 at 880°C. At 600°C the MgO peaks formed in C-43.

The 2θ angles of the characteristic peaks of portlandite and calcite were found to move towards lower values, thus the respective basal spacings *d*(*hkl*)

were increasing (Table 4), which is analyzed separately [27, 28].

Conclusions

The comparison of the SH test results of the freshly hydrated cement pastes and of those obtained by DTA/DTG/TG, MS, IR and XRD of the aged ones (5–6 years), leads to the conclusions presented below. The discussion is supplemented by the SEM and TEM study of the 1-year old paste C-43, presented elsewhere [1–2] and of the less dense paste [27].

Main components found in the hydrated and aged pastes were the sorbed water, the CSH gel, portlandite and carbonates. The content of these hydration products indicated significant differences between the fresh stronger paste C-43 and the weaker one, C-33 (of a smaller specific surface), where it was lower, except for the carbonate content. These differences were generally less apparent after ageing.

The sorbed water content was in the fresh paste C-43 by 1.3 times higher than in C-33 (110°C). After ageing it evolved at 185 and 155°C from C-33 and C-43, respectively and its value decreased by 0.58–0.75, being partially transformed into a high temperature form (lost at 500–700°C which included some CO$_2$); the difference between both pastes became almost non-existent.

The organic matter development caused an apparent increase with ageing of the hydrate +CSH gel water content of paste C-43.

Portlandite water content was in fresh C-43 almost twice that in C-33 and it changed little with ageing if measured in argon. Its decomposition proceeded in air at 470°C, and was dependent on measurement conditions (450°C in argon, 400°C in vacuum, peak position). Aged pastes contained big portlandite crystals of a high crystallinity (XRD), as outer products (SEM) and nanocrystals were also present (TEM).

Sensitivity to carbonation in the fresh pastes, was almost twice higher in C-33 than in C-43 (SH, 600–800°C). This value increased on ageing by about 1.4 in C-33, by 2.4 in C-43 (TG, 685–760°C) and the difference between both pastes disappeared.

The carbonates were formed mainly on ageing and less on heating. They were present in the hydrated and aged cement paste already at room temperature and their content changed little with its increase (IR). Initially, mainly in nanocrystalline form (XRD, TEM), they grew on heating to larger units (XRD). At 500–600°C in air their content possibly increased due to carbonation of portlandite and/or of the CSH gel components (TG).

Calcium carbonates are present as calcite and as the metastable high pressure polymorphs (aragonite

and vaterite, mainly in C-33, XRD), possibly containing some HCO_3^- ions and/or OH^- ions and/or water molecules (hydrates). Aragonite peaks were found at 3.40, 2.37 and 1.98 Å, vaterite peaks at 3.29, 2.74, 2.10, 2.06 and 1.82 Å.

About 500°C in vacuum (MS) equal amounts of CO_2 and H_2O were evolved from the aged paste, whereas the peaks of CO_2 loss were observed at about 550, 630 and 750°C and those of H_2O at 120, 350 (in C-33) and 400°C. This is interpreted as (i) dehydration of CSH gel component (up to 400°C), (ii) their dehydroxylation above 500°C, (iii) decomposition of some form of carbonate hydrate or hydrocarbonate and of calcite. The three peaks of CO_2 escape with simultaneous H_2O evaporation, indicate the presence of three forms of carbonates, which needs a further study.

The paste C-43 pretreated with acetone indicated an exceptionally high mass loss between 480 and 710°C (11.1%), in analogy to the paste of a low density [27]. Otherwise the respective mass loss was higher in C-33 than in C-43. Acetone may be adsorbed on the edges of the lamellae, preventing contact bonds formation on drying. This facilitates the escape of internal water (dehydroxylation) and escape of some anions from the crystal lattice. All the thermal effects were observed at lower temperatures in argon than in air and even at lower ones in vacuum.

The mass loss up to 800°C increased with ageing from 25.5 to 28.6–29.4% (C-33) and from 28.8 to 30.0–35.9% (C-43). The mass loss up to 1000°C was 29.9–30.4% in C-33; it was highly dependent on measurement conditions in C-43, i.e. 31.8% in air, 33.3% in argon and 38.1% after acetone pretreatment.

The most suitable method for quantitative study of the products of cement hydration seems to be the DTG/TG test, supplemented either by evolved gas analysis (EGA) or by MS. XRD study alone may give erroneous information on the quantitative content of particular components as the peak intensity depends on size of crystallites and on their crystallinity.

Acknowledgements

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