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THERMO XRD-ANALYSIS OF TWO AGED CEMENT PASTES

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Two hydrated and aged cement pastes from India (NCB), *w*/*c*=0.4, of a similar chemical composition but of a different specific surface and different strength (OPC, C-33 and C-43), hydrated at *w*/*c*=0.4 for 1 month, were studied by XRD after 1 year and 5–6 year ageing on contact with air. They were tested by static heating (SH) in fresh state, and by DTA/DTG/TG, IR and mass spectrometry (MS), after ageing, presented elsewhere.

The main XRD peaks of (*i*) portlandite were decreasing with *T* and disappearing about 450°C, (*ii*) calcite peak at room *T* was small and broad, it increased gradually, especially after portlandite disappearance; above 600°C it was lowered and it was lost above 700°C.

Important variation in the *d*(001) of portlandite with ageing was observed, exceeding the standard value of *d*(001)= 4.895 Å (72-0156). It was higher in the paste C-33 (4.925–4.936 Å), containing more carbonates, than in the paste C-43 (4.916–4.927 Å). Small variations only were found in the value of *d*(101), i.e. 2.627–2.635 Å (nominally 2.622 Å), whereas the *d*(104) of calcite could be used as internal standard and other calcium carbonates (vaterite and aragonite) showed a small variation only.

The increase in *d*(*hkl*) with temperature was straight linear (in portlandite Δ*d*(001)=0.095 Å, at 30–400°C) and the thermal expansion coefficient estimated thereform was high ($4.75–4.95\cdot10^{-5}$ K^{-1}). Close to the *T* of decomposition the Δ*d*/Δ*T* became steeper.

The thermal variation of *d*(104)=3.035 Å of calcite (Δ*d*=0.015 Å at 30–400°C) was smaller than that of *d*(101) of portlandite (Δ*d*=0.025 Å at 30–400°C) and was similar in C-33 and C-43. The thermal expansion coefficient was $1.54\cdot10^{-5}$ K^{-1}, thus higher than the reported $\alpha_a=0.65\cdot10^{-5}$ K^{-1}.

Keywords: *ageing of cement paste, aragonite, calcite, cement hydration, d(hkl) variation, portlandite, thermal expansion, vaterite, XRD*

Introduction

An unusually high *d*(001) spacing of portlandite was observed, when studying the hydration products of two aged cement pastes, which was less the case for *d*(101) spacing [1]. Also the increase on heating of *d*(001) and the thermal expansion coefficient was high and was more pronounced than those of *d*(101). These problems are analyzed below in detail.

Ordinary Portland cement (OPC) is composed mainly of alite [$C_3S=3CaO\cdot SiO_2$] and belite=larnite [$C_2S=2CaO\cdot SiO_2$], hydrating to the C–S–H gel [kCaO$\cdot m$SiO$_2\cdot n$H$_2$O], which is believed to create the paste strength. The other main product of the reaction with water is portlandite [$CH=Ca(OH)_2=CaO\cdot H_2O$], which on ageing and at availability of CO_2 from air, is carbonated to $CaCO_3$, i.e. calcite, aragonite and vaterite. These compounds were found in two aged cement pastes, discussed here. No consideration is given to other products, e.g. AFm, AFt.

Both these cement pastes contained qualitatively similar hydration products (sorbed water, hydrates, C–S–H gel, portlandite, carbonates and unhydrated silicates), their quantitative composition being different. On heating of the hydrated paste, the alite (C_3S), belite (C_2S) and lime (CaO) developed, whereas the remaining compounds decomposed. Of the highest interest here are portlandite and carbonates, i.e. calcite and metastable aragonite and vaterite, which transform above 400°C into stable calcite [2].

The transformation of synthetic aragonite to calcite occurred at 723 K (450°C) as found by Lucas *et al*. [3]. From the variation in basal spacings with temperature the anisotropic thermal expansion coefficients were calculated within the temperature ranges 291–700 and 800–900 K for aragonite and calcite respectively. These values are compared below with those estimated for the aged cement paste.

Experimental

Materials

Cement

Two OPC from India of grade 33 and 43 were supplied in form of standard cubes (IS:8112-1989) by NCB, New Delhi. Their chemical composition was similar, except MgO content (Table 1). They differed

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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
C43	61.0	20.9	5.3	3.1	3.6	0.89	1.5	0.45	2.7

*LOI is the loss on ignition

in strength, as they differed in specific surface, which in hydrated state was 146 and 166 $m^2 g^{-1}$ in C-33 and C-43, respectively [4].

Both pastes were prepared at *w*/*c*=0.4 and they were hydrated for 1 month at room temperature and either air dried or treated with acetone and air dried (ac).

Hydration and ageing products in the OPC pastes

The hydration products in the hydrated pastes, determined previously and published elsewhere [1], are summarized below. Thus their content as measured by static heating (SH) and TG, is shown in Table 2.

Sorbed water, which in fresh samples was measured at 110°C, in the aged ones was bound more strongly and got lost partly up to 155–185°C and partly as high as at 500–700°C. This contribution was interpreted as dehydroxylation of jennite-like phase and/or dehydration of some carbonate hydroxy hydrates of unknown composition.

The main crystalline compounds found in the aged paste were:

- portlandite (*P*), decreasing with *T* and disappearing at about 450–470°C; its content was higher in C-43 than in C-33 (XRD)
- calcite (C) of a low and broad XRD peak, increasing with *T* above 400 up to about 700°C and disappearing at more elevated *T*s; it was higher in C-33 than in C-43 (XRD and IR). A slight decrease in the calcite XRD peak intensity was observed about 200°C. IR spectroscopy indicated appreciable amount of CO_3^{2-} both at room *T* and at higher ones. Carbonate content decreased at 400°C in C-33 and increased in C-43 (IR)
- aragonite (A) and vaterite (V) as metastable carbonates, were transformed into calcite above 400°C (450°C in Lucas *et al.* [3], whereas [5] indicates 520°C for aragonite-calcite transition)

By mass spectrometry (MS) two peaks of water escape were found in C-33 (~110 and ~300°C). Above 300°C in vacuum there escaped simultaneously H_2O and CO_2. The peaks of decarbonation of C-43 were found at three temperatures, i.e. 560, 630 and 750°C, which in C-33 was less discernible.

The *T* of decomposition of the respective compound varied with environment (air or argon in DTG and vacuum in MS). The necessary energy was most probably dependent on the availability of CO_2 (its partial pressure) and/or CO_3^{2-} (its concentration), Table 3.

Methods

XRD study of the hydration products was done by the following methods:

Table 2 Content of hydration products in two cement pastes as estimated by SH and TG in air (Δ*M* in mass/mass%) the mass loss related to the mass after heating

Paste	Test		Sorbed water	CSH gel and hydrates	Portlandite water	High *T* Δ*M*	CO_2 of carbonates	Residual	Δ*M*<0
fresh	SH air								
C-33		*T*/°C Δ*M*	110 10.3	110–400 6.4	400–600 3.1	–	600–800 5.7		
C43		*T*/°C Δ*M*	110 13.2	110–400 6.7	400–600 5.6		600–800 3.3		
aged	TG air								
C-33		*T*/°C Δ*M*	185 7.5	185–460 5.7	460–485 2.6	485–700 5.2	700–760 7.8	to 1000 1.3	485–585 –0.2
C-43		*T*/°C Δ*M*	155 7.6	155–450 8.7	450–490 3.2	490–685 2.6	685–750 7.9	to 1000 1.8	490–600 –1.2
aged	TG air								
C-33 ac		*T*/°C Δ*M*	185 8.3	185–460 5.9	460–490 3.1	490–680 4.3	680–750 7.7	to 1000 1.1	
C-43 ac		*T*/°C Δ*M*	160 8.0	160–460 7.7	460–480 2.3	480–710 11.1	710–740 6.8	to 1000 2.2	480–530 –0.9

Table 3 Temperature (°C) of decomposition (TG)

Nominal	Portlandite		Calcite	
	580°C [5]		898.6°C [5]	
Atmosphere	C-33	C-43	C-33	C-43
air	470	470	740	720
argon	450	450	710	680
vacuum	400	400	630	630

- after 1 year ageing (Siemens Kristalloflex with graphite Monochromator CuK_α and the computer SICOMP PC 16-20 with files of standard minerals JCPDS-ICDD)
- after 5–6 year ageing (Philips X-pert, with a high *T* chamber ANTON PARR, HTK 1200, X'celerator, copper tube and θ–θ goniometer), at *T*s corresponding to the peak on the DTA/DTG curve, to its start and to its tail. The heating rate was 5 K min^{-1} and the goniometer rate was 5.4° min^{-1} at the total time 12 min 18 s for the 2θ range 5 to 65° and detector range 2.118°

The freshly hydrated pastes were tested by static heating and the 1 year old pastes were investigated by (XRD) SEM and HRTEM [4, 6]. The 5–6 year old pastes were tested by (XRD) DTA/DTG/TG, IR and MS (mass spectrometry), which results are presented elsewhere in detail [1] and were summarized above. The results of XRD will be presented and analyzed here, concerning the change in basal spacing depending on the paste quality, on the ageing time and on temperature.

Results

Variability in d(hkl) spacing with pretreatment and ageing

In Figs 1a and c the results of XRD study of the paste C-33 and C-43 at room *T* are presented and in Figs 1b and 1d those obtained at variable *T*, corresponding to start, peak and tail of the DTG curve. The values of the selected *d*(*hkl*) spacings are indicated in Tables 4 and 6.

Portlandite

The increase in *d*(*hkl*) spacings, as compared to the nominal ones, was observed and it was dependent on the pretreatment of the hydrated paste on its age and on measurement conditions (Table 4). The full expansion of *d*(001) did not occur after 1 year: in C-33 (4.925 Å), but it followed the wetting and drying procedure, *d*(001) achieving 4.937 Å, as compared to the nominal 4.895 Å. Acetone pretreatment resulted in a smaller *d*(001) value, which increased as well after wetting and drying (4.902 and 4.912 Å, respectively). Both the air dry and acetone pretreated pastes indicated after 5 year ageing the same *d*(001) value of 4.936 Å, corresponding to full expansion.

In C-43 the *d*(001) was similar after 1 and 5 year ageing (4.916 Å), and it increased after wetting and

Table 4 *d*(*hkl*) (Å) of portlandite

In aged paste C-33							
C-33 – 1 year		C-33 – 1 year (ac)		C-33 5 year		Nominal (72-156)	
	wet–dry		wet–dry		(ac)	*d*(*hkl*)	*hkl*
a		b		c		d	
4.925	4.937	4.902	4.912	4.936	4.936	4.895	(001)
2.631	2.633	2.622	2.625	2.635	2.633	2.622	(101)
In aged paste C-43							
C-43 – 1 year		C-43 – 1 year (ac)		C-43 – 5 year		nominal (72-156)	
	wet–dry		wet–dry		(ac)	*d*(*hkl*)	*hkl*
4.916	4.927	4.914	4.927	4.916	4.916	4.895	(001)
2.627	~2.63	2.631	2.629	2.630	2.630	2.622	(101)

Table 5 Crystallographic parameters of portlandite, syn. (hexagonal)

File Nr.	*a*/Å	*b*/Å	*c*/Å	*V*/Å^3	*d*(001)	*d*(101)
04-0733	3.5930	3.5930	4.9090	54.88	4.900	2.628
44-1481	3.5899	3.5899	4.9160	54.87	4.922	2.627
72-0156	3.5853	3.5853	4.8950	54.49	4.895	2.622
87-0673	3.5890	3.5890	4.9110	54.78	4.911	2.626

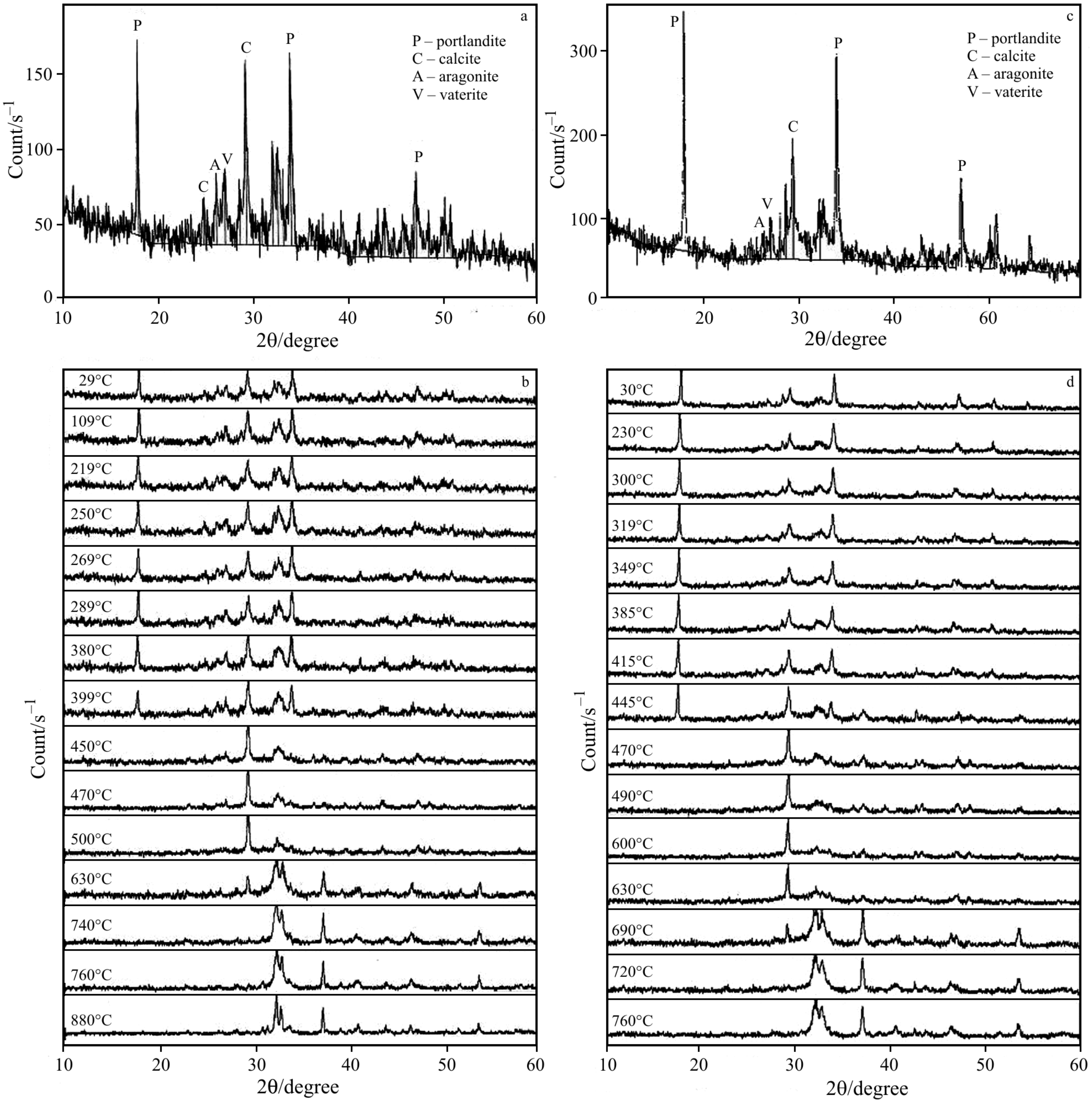

Fig. 1 Results of XRD study: XRD traces obtained at room temperature of a – C-33 and c – C-43. XRD traces at elevated *T*s of b – C-33 and d – C-43

drying to 4.927 Å. Acetone pretreatment did not change the measured values.

The variability of *d*(101) and of other *d*(*hkl*) spacings was much smaller, but its tendency was similar as in case of *d*(001).

The variability in *d*(001) spacing was found also in standard files. The observed change in spacings of portlandite, which was formed on paste hydration, was though higher than the differences of reported nominal values found in 4 files JCPDS-ICDD, Table 5. The maximum difference was between 4.922 Å (44-1481) and 4.895 Å (72-0156), which was assumed as reference.

Carbonates

The *d*(104) spacing of calcite, formed in hydrated and aged pastes, was close to the nominal value and indicated almost no variability with paste age and its pretreatment (Table 6), thus this spacing could be used as internal standard.

The variability in aragonite of *d*(111) and *d*(221) was only slightly higher than that of calcite. Vaterite in C-33 indicated an increase in some *d*(112) values.

Table 6 $d(hkl)$ (Å) of carbonates

In aged paste C-33							
C-33 – 1 year		C-33 – 1 year (ac)		C-33 – 5 year		Standard	
	wet–dry		wet–dry		(ac)	$d(hkl)$	hkl
calcite							
3.038	3.038	3.026	3.035	3.046	3.043	3.035	(104)
2.284	2.287	2.282	2.282	2.288		2.285	(113)
aragonite							
3.403	3.394	–	–	3.405		3.397	(111)
1.982	1.982	1.982	1.978	1.980		1.977	(221)
vaterite							
3.318	3.296	3.318	3.289	3.296		3.294	(112)
2.063	2.062	–		2.064		2.063	(300)
1.824	1.822	1.826	1.822	1.824		1.820	(118)
In aged paste C-43							
C-43 – 1 year		C-43 – 1 year (ac)		C-43 – 5 year		Standard	
	wet–dry		wet–dry		(ac)	$d(hkl)$	hkl
calcite							
3.032	3.036	3.036	3.037	3.035	3.035	3.035	(104)
2.285	2.285	2.284	2.290	2.285	2.285	2.285	(113)
aragonite							
3.404	3.396	3.395	3.403	3.394	3.394	3.397	(111)
1.975	1.976	1.985		1.984	1.984	1.977	(221)
vaterite							
3.295	3.289	3.283	3.295	3.291	3.291	3.294	(112)
2.061	2.066	2.057	2.053	2.060	2.060	2.063	(300)
1.822	1.821	1.826	1.829	1.820	1.815	1.820	(118)

Table 7 Regression lines for the correlation between the change in $d(hkl)$ (Å) and the temperature; $\Delta d(hkl)=A+BT$

Compound	Paste	T_{range}/°C	$d_0(hkl)$	A+B	R	SD
portlandite	C-33 (ac)	30–450	4.936 (001)	$-0.00989+2.3457\cdot10^{-4}$	0.9968	0.00254
	C-43 (ac)	30–450	4.916 (001)	$-0.00989+2.3457\cdot10^{-4}$	0.9968	0.00254
	C-33 (ac)	30–400	2.633(101)	$-0.0017+6.5157\cdot10^{-5}$	0.98908	0.00132
calcite	C-43 (ac)	30–400	2.630 (101)	$-0.0021+5.2869\cdot10^{-5}$	0.99023	0.00107
	C-33 and C-43 (ac)	30–700	3.043 (104), 3.035 (104)	$-0.00257+4.68555\cdot10^{-5}$	0.96758	0.00199

In C-43 the $d(hkl)$ of calcite and aragonite were about equal the nominal ones whereas a tendency of their lowering was observed in vaterite.

Although the standard crystallographic parameters of portlandite were presented in 4 files varying in values, the calcium carbonates are characterized either by a single standard file or by files of virtually identical values (calcite).

Variability in d(hkl) spacing with temperature

The increase in $d(001)$ spacing of portlandite with temperature is shown in Figs 2a and b and that of $d(101)$, in Figs 2c and d, for C-33 and C-43, respectively.

Within a certain temperature range T_1 to T_2 the increase in $d(hkl)$ with T was straight linear. In some cases of compounds formed at a high T:

- below T_1 there was no thermal expansion and $d(hkl)$=const.
- above T_2 this value exceeded the calculated correlation (Figs 3a and b)

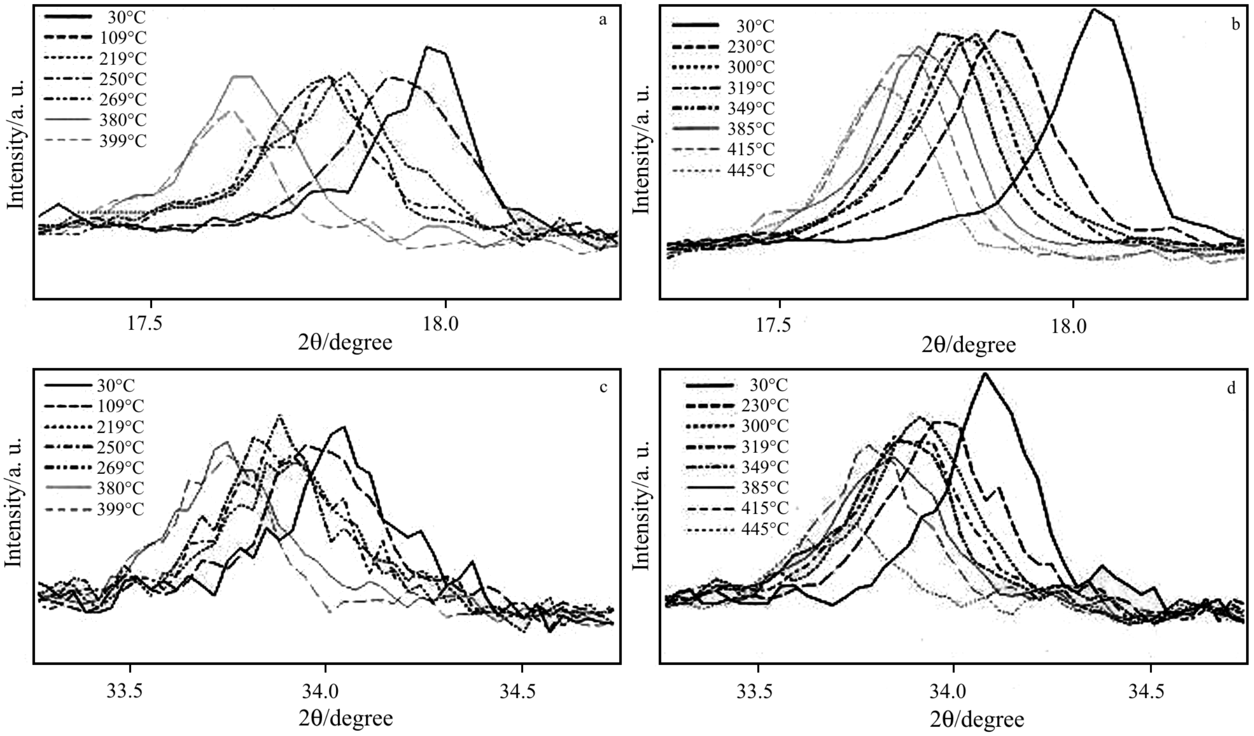

Fig. 2 The increase in basal spacing *d*(001) of portlandite with temperature: a – C-33 and b – C-43, and that of *d*(101), in c – C-33 and d – C-43

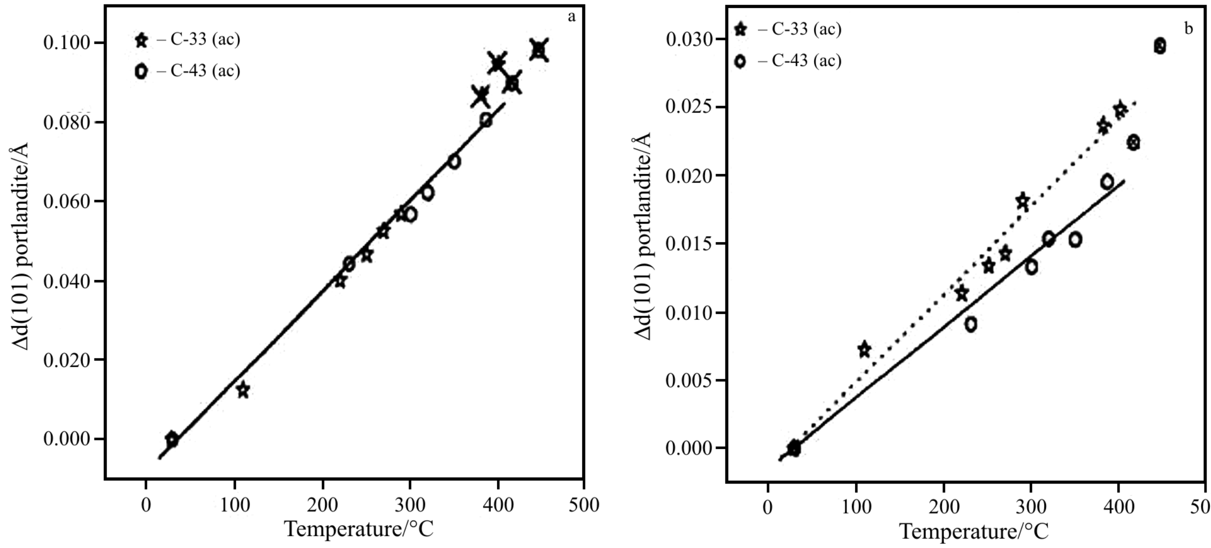

Fig. 3 Correlations between the increase in basal spacings and the *T* for a – C-33 and b – C-43

Thus the correlations between the increase in spacing Δ*d*(*hkl*) and temperature were calculated and they are presented in Table 7 and in Figs 3a and b. The data for the highest temperature, departing from the straight linear relation, were excluded from calculation, due to the postulated difference in the physical state of the heated paste (a high amplitude of thermal vibrations).

The calculated thermal expansion coefficients, α, are presented in Table 8 and compared with values published in the literature.

α(001) of portlandite is much higher and α(101) is higher than the α(104) of calcite and than the thermal expansion coefficient reported in the literature.

Table 8 Thermal expansion coefficient (*i*) calculated as [$\alpha(hkl)=B/d_0(hkl)$] and (*ii*) reported in the literature

Compound	Paste	T_{range}/°C	$\alpha(hkl)\cdot 10^5$/K^{-1}	α reported $\cdot 10^{-5}$/K^{-1}	Reference
portlandite	C-33 (ac)	30–450	4.75 (001)		
	C-43 (ac)		4.95 (001)		
	C-33 (ac)	30–400	2.48 (101)		
	C-43 (ac)	30–400	2.01 (101)		
calcite	C-33 and C-43 (ac)	30–700	1.54 (104)	$\alpha_a=0.65$	[3]
			1.54 (104)	$\alpha_c=3.85$	(800–900°C)
aragonite				$\alpha_a=0.88\pm0.11$	[3]
				$\alpha_b=1.92\pm0.17$	
				$<\alpha>_{298-1000\ K}=6.75$	[7]

Discussion and conclusions

The XRD study of two hydrated and aged cement pastes (in contact with air) indicates the following:

- the *d*(001) of portlandite, measured by XRD in cement pastes, depends on their quality and age. Expansion of the *d*(001) spacing follows the ageing, increasing with ageing time of the low strength paste (1 to 5 years), which contained more carbonates. In the paste of the higher strength the expansion was lower and it was terminated after 1 year. Wetting and drying of this paste caused a maximum expansion, lower than that in the weaker paste
- the acetone pretreatment lowered the expansion but after wetting and drying the result was the same as in the unpretreated paste
- also the crystallographic parameters of portlandite syn. are reported in four standard files, indicating different values, but the variations are lower than those in the hydrated pastes
- on heating a straight linear relation was found between the *d*(001) spacing of portlandite and temperature, *T*. The thermal expansion coefficient, calculated therefrom, was high, indicating a low lattice energy
- other *d*(*hkl*) spacings of portlandite showed a lower expansion with ageing and heating
- also the *d*(*hkl*) spacings of calcite, aragonite and vaterite were close to the nominal values and were little dependent on ageing. The measured increase in the (*hkl*) spacings with *T* was much smaller than that of portlandite. Nevertheless the thermal expansion coefficient calculated therefrom was higher than that reported in the literature
- calcite [*d*(104) and *d*(113)] could be used as internal standard; aragonite [*d*(111) and *d*(221)] showed a slight increase with age, whereas vaterite [*d*(112) and *d*(300)] indicated in some cases a tendency of lowering the basal spacing with time (partial substitution of CO_3^{2-} ions by the smaller OH^- ions and/or vacancies in the crystal lattice) and its crystallinity was low (HRTEM)
- the quantity of portlandite, which was formed on hydration depends on cement quality (increases with strength). The sensitivity to carbonation deduced from the content of carbonate (SH) and from the *d*(001) spacing decreases with strength
- it is postulated here, that the OH^- ions in portlandite are with ageing gradually substituted by the CO_3^{2-} ions, which have an about twice bigger diameter. This causes an increase in the *d*(001) spacing, increase in the thermal expansion coefficient and a decrease in the temperature of decomposition, as the lattice energy is lowered. Similarly in calcite, initially some OH^- ions remain. They are smaller than CO_3^{2-}, thus they do not cause any significant change in the (104) spacing, but result in lowering of the energy (temperature) necessary for the decomposition. This will be discussed in a separate paper

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