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In vitro aging of a calcium phosphate cement

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Cement samples made of β-tricalcium phoshate (β-TCP), phosphoric acid (PA) and water mixtures were incubated in several aqueous solutions to determine their stability over time. The effects of the cement composition and the incubating temperature were investigated in more detail. The cement samples contained mostly dicalcium phosphate dihydrate (DCPD) and remnants of β-TCP crystals. Depending on the initial cement composition, a certain amount of dicalcium phosphate (DCP) crystals were formed. The larger the initial PA concentration, the larger the DCP amount. After setting, the cement composition was stable for at least 16 days up to 60 °C. Above that temperature, the DCPD crystals decomposed into DCP crystals. The latter reaction provoked a decrease of the pH of the incubation solution, phenomenon expected for a cement sample containing an excess of PA. As the cement samples contained an excess of β-TCP, it was postulated that β-TCP crystals became so covered by DCP or DCPD crystals during setting that the setting reaction was stopped prematurely. The latter phenomenon gave a good explanation for the low pH values measured in the incubation solutions.

1. Introduction

Last decade, Lemaître *et al.* [1] and Mirtchi *et al.* [2] presented a new calcium phosphate cement (CPC) made of β-tricalcium phosphate [$\beta\text{-}Ca_3(PO_4)_2$; β-TCP], monocalcium phosphate monohydrate [$Ca(H_2PO_4)_2 \cdot H_2O$; MCPM] and water mixtures. The reaction product is dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$; DCPD)

$$\beta\text{-}Ca_3(PO_4)_2 + Ca(H_2PO_4)_2 \cdot H_2O + 7H_2O \rightarrow 4CaHPO_4 \cdot 2H_2O \quad (1)$$

In vivo studies have shown that this cement is biocompatible, resorbable and osteoconductive [3, 4], hence representing an excellent bone substitute. Depending on the surrounding conditions, DCPD decomposes into its anhydrous form ($CaHPO_4$; DCP) according to the following reaction

$$CaHPO_4 \cdot 2H_2O \rightarrow CaHPO_4 + 2H_2O \quad (2)$$

In a dry environment, pure DCPD decomposes at around 109 °C [5]. This decomposition temperature was also observed for a DCPD-containing CPC made of β-TCP, phosphoric acid, sulfuric acid and water mixtures [6]. However, a CPC made of β-TCP, MCPM and water mixtures decomposed above 40 °C [2].

The presence of water is known to lower the decomposition temperature [7, 8]. For example, DCPD tablets decomposed into DCP at 45 °C and 75% relative humidity [7]. Furthermore, according to Bassett, DCPD should decompose in an aqueous solution above a temperature of 36–40 °C [8].

A low pH in the aqueous solution can also trigger DCPD decomposition [9, 10]. In their study on the precipitation of calcium phosphates from electrolyte solutions at 37 °C, Kosar-Grasic *et al.* [9] detected DCP crystals at a pH smaller than 4. A lower pH resulted in a faster transformation. Martin and Brown [10] mentioned that: ‘‘under acidic conditions in the presence of MCPM, DCPD readily converted to DCP below 37 °C’’. DCP was also observed in CPC samples prepared at 25 °C and containing an excess acidic phase [11, 12]. However, it is not known what temperature was reached within the cement samples during setting.

The pH, the presence of water, time and temperature thus all have a strong effect on the decomposition of DCPD into DCP. This large number of factors probably explains why the actual results on this decomposition reaction are sometimes contradictory. Another reason is that DCPD precipitates more easily than DCP, even though DCP is more stable at atmospheric pressure than DCPD [13]. According to the thermodynamic data determined by Brown and co-workers [14, 15], DCP is more stable than DCPD above a temperature of 0 °C. DCPD has been reported to precipitate at 55 °C [10] and even at 70 °C [16]. In the latter study [16], no DCP precipitated below 60 °C, even though DCP crystals were

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present in the solution. However, Fulmer and Brown [17] reported the simultaneous precipitation of DCP and DCPD at 45 °C.

In experiments done on CPC made of β-TCP–MCPM–water mixtures, DCP was found in samples aged at 37 °C, in PBS for eight days [18]. In other experiments done with similar samples, no decomposition could be observed after aging for five days [18]. To use the CPC *in vivo* this decomposition reaction has to be well known. The decomposition reaction of DCPD into DCP is indeed detrimental to the mechanical properties of CPC [12]. Moreover, the presence of DCP in the CPC may modify its *in vivo* behavior. Therefore, the *in vitro* aging behavior of CPC was investigated here.

To simplify the cement composition, MCPM can be replaced by phosphoric acid (PA) [12]. The setting reaction becomes

$$\beta\text{-}Ca_3(PO_4)_2 + H_3PO_4 + 6H_2O \rightarrow 3CaHPO_4 \cdot 2H_2O \tag{3}$$

This cement has been commonly used as a model for CPC made of MCPM–TCP–water mixtures [11–12, 19]. Despite the presence of phosphoric acid, the pH evolution of this cement is very similar to that of an MCPM-containing cement [11]. The only difference is the very low pH measured during the first 20 s of mixing. Keeping the same overall composition, the setting time of this cement is longer than that of the MCPM–TCP cements [6], as suggested by pH measurements [11]. The tensile strength is also larger due to higher homogeneity of the microstructure [6].

2. Materials and methods

2.1. Sample preparation

The cement samples were prepared by mixing thoroughly 1.5 g of dry β-TCP powder (Art. 21218, lot 31760/1 396; Fluka, Buchs, Switzerland) with 2 ml PA solution (Art. 79′621, lot 332720/1 1193; Fluka). The paste was mixed for 30 s with a spatula, and then filled into a syringe whose tip had been previously cut. After hardening, the samples were pushed out of the syringe and incubated in 10 ml deionized water. At the end of the incubation time, the samples were retrieved and the pH of the incubation solution was measured. The samples were then dried at room temperature and calcined at 500 °C to determine their weight loss.

Three series of experiments were carried out. In the first series, the effects of incubation time (6, 12, 24, 48, 96, 192 and 384 h), cement composition (PA 1.6, 2.0 and 2.4 M) and incubation temperature (23 and 37 °C) were investigated. In the second and third series (PA 2.0 M), the effect of incubation temperature was studied in more detail. In the second series, samples were aged at 37, 40 and 45 °C for 6, 12, 24, 48, 96, 192 and 384 h. In the third series, samples were aged at 50, 60 and 70 °C for 6, 24, 96 and 384 h.

2.2. Characterization

The pH of the aging solution was measured 30 min after retrieving the sample in order to allow the solution to cool down. The porosity measurements were made using Archimedes' principle as described in [19]. Each sample was first impregnated under vacuum (approximately 10 kPa) with 2-propanol. The volume of the open porosity was calculated from the difference in weight before and after impregnation. The apparent volume of the sample was calculated from the increase in weight measured when the sample was dipped into a beaker lying on the pan of a balance and filled with 2-propanol. Assuming that the samples had no closed porosity (as evidenced in [19]), the total porosity can be easily calculated. The gravimetric loss of the cement samples was measured by means of a muffle furnace. The samples were calcined for 1 h at 500 °C. In the latter conditions, DCPD and DCP are decomposed according to the following reactions

$$2CaHPO_4 \cdot 2H_2O \rightarrow Ca_2P_2O_7 + 5H_2O \tag{4}$$

$$2CaHPO_4 \rightarrow Ca_2P_2O_7 + H_2O \tag{5}$$

The weight losses corresponding to Equations 4 and 5 are 26.1 and 6.6% w/w, respectively. Therefore, if the cement contains only β-TCP, DCPD and DCP, the lower the cement weight loss, the larger the amount of DCP present in the cement sample. Assuming that all the PA reacts with β-TCP to form either DCPD or DCP, the composition of the cement samples can be determined [6].

2.3. Factorial design of experiments $2^{(7-1)}$

In a first attempt to understand the decomposition reaction of DCPD into DCP better, a factorial design of experiments $2^{(7-1)}$ was performed. The factors were: (A) the aging time (1–96 h), (B) the aging buffer (water, pH 7.4 PBS), (C) the presence of gentamicin sulfate (GS, 0–5% w/w), (D) the PA concentration (2.0–2.4 M), (E) the drying atmosphere (air, atmosphere in equilibrium with a saturated $CaCl_2$ solution), (F) the amount of $Na_2H_2P_2O_7$ (NaPP) dissolved in the mixing liquid (0–3.3 mmol), and (G) the aging temperature (23–37 °C). The factor G was confounded with the interaction ABCDEF. The basic cement composition was 1.5 g β-TCP and 2.0 ml mixing liquid. The aging solution had a volume of 10 ml. The pH of the aging solution and the weight loss of the samples after aging were the two properties investigated. Analysis of the pH measurements was difficult due to the insufficient buffer capacity of the aging solution. Therefore, the buffer solution of some of the samples prepared with PA 2.4 M had a high pH after 1 h (around 6) and a low pH after 96 h (around 4.5 – ABD interaction). As GS has a certain buffer capacity, a significant interaction ABCD ($p < 0.05$) was also measured. Five factors (A, B, C, D, E) and ten interactions had a significant effect on the weight loss. However, the absolute effects were all very limited ($< 0.9\%$), suggesting that none of the factors investigated had a significant effect on the decomposition reaction of DCPD into DCP.

3. Results

The solubility diagram of selected calcium phosphates is shown in Fig. 1. This solubility diagram has been

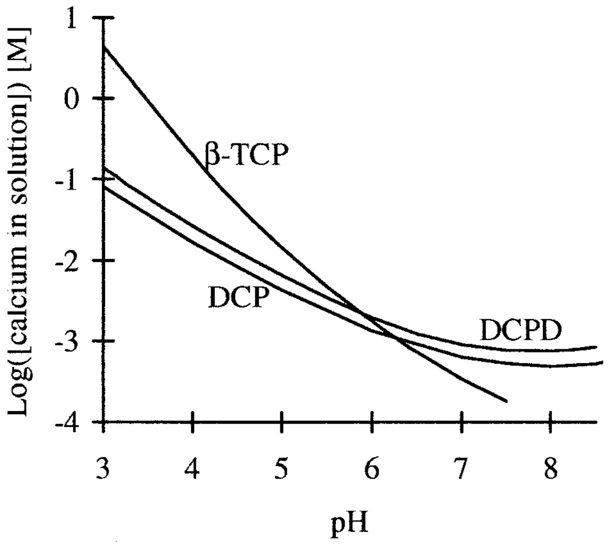

Figure 1 Solubility diagram of selected calcium phosphates in water and at 25 °C [14, 15, 20]. The solubility is expressed as the total molar concentration of calcium ions dissolved in solution.

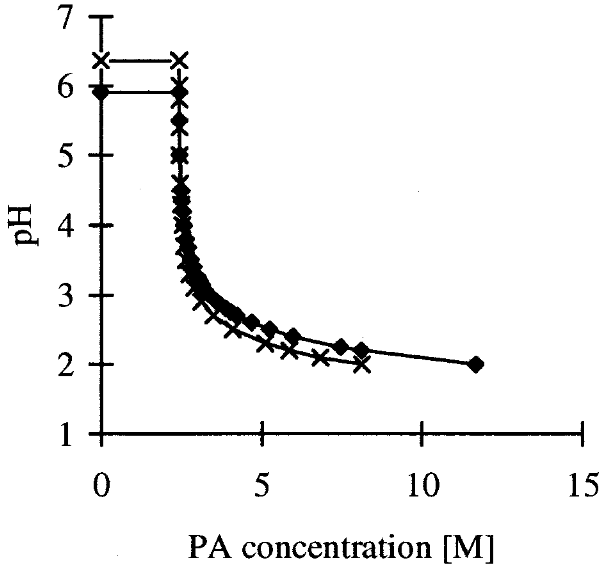

Figure 2 Calculation of the equilibrium pH of a cement sample made of 1.5 g β-TCP and 2 ml PA solution and incubated in 10 ml deionized water. It was assumed that the end-product of the setting reaction was either DCPD (◆) or DCP (×). The discontinuities along the curve occur when PA is in excess according to Equation 3.

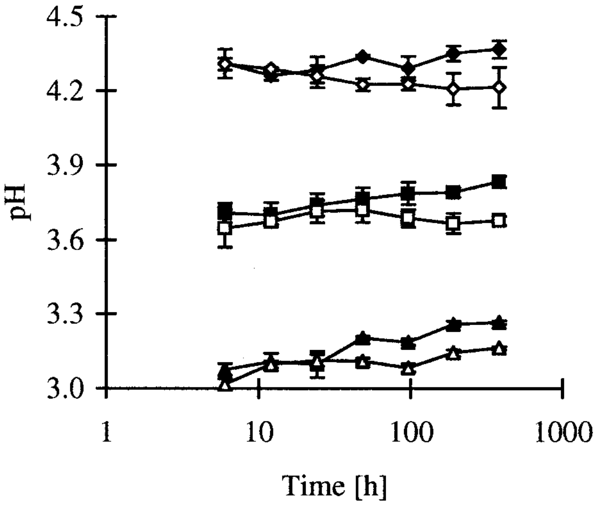

Figure 3 pH of the incubation solution at different times. Composition of the cement samples: 1.5 g β-TCP and 2 ml H_3PO_4 solution. Temperature and H_3PO_4 concentration: (◆) 23 °C, 1.6 M; (◇) 37 °C, 1.6 M; (■) 23 °C, 2.0 M; (□) 37 °C, 2.0 M; (▲) 23 °C, 2.4 M; (△) 37 °C, 2.4 M. The error bars correspond to the 95% confidence interval on the mean.

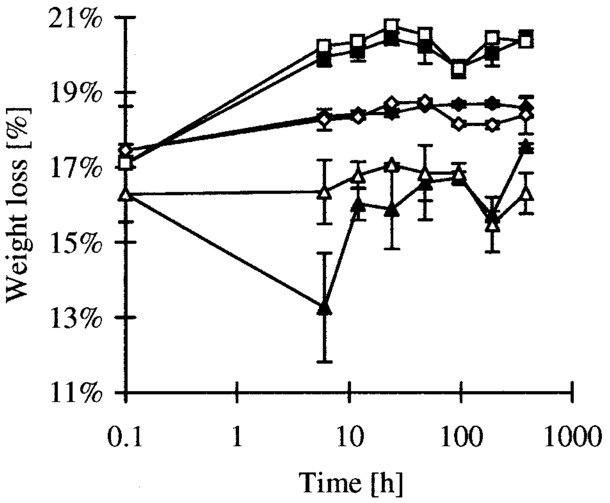

Figure 4 Weight loss of cement specimens as a function of incubation time. The results given for the time "0.1 h" correspond to the samples dried without previous incubation. Composition of the cement samples: 1.5 g β-TCP and 2 ml H_3PO_4 solution. Temperature and H_3PO_4 concentration: (◆) 23 °C, 1.6 M; (◇;) 37 °C, 1.6 M; (■) 23 °C, 2.0 M; (□) 37 °C, 2.0 M; (▲) 23 °C, 2.4 M; (△) 37 °C, 2.4 M. The error bars correspond to the 95% confidence interval on the mean.

obtained using the thermodynamic data of Brown and co-workers [14, 15, 20]. The equilibrium pH between DCPD and β-TCP and between DCP and β-TCP is 5.88 and 6.36, respectively [20]. Using the same solubility data, the equilibrium pH of the cement can be predicted (see the appendix). The larger the PA concentration, the lower the equilibrium pH (Fig. 2). When there is an excess acidic phase, the equilibrium pH DCP–solution is lower than that of DCPD–solution.

3.1. Effect of the PA concentration

The pH of the incubation solution decreased with an increase of the PA concentration in the mixing liquid (Fig. 3). However, the incubation temperature and time had very little effect on the pH. These two factors interacted to modify the solution pH slightly. After more than one day of aging, the pH values measured in the solutions incubated at 37 °C were lower than those measured in the solutions incubated at 23 °C (Fig. 3).

The PA amount used to prepare the cement had a large effect on the cement weight loss (Fig. 4). Decreasing weight losses were measured in samples made with the following concentrations (in decreasing order): 2.0, 1.6 and 2.4 M. The weight losses did not depend on the incubation time, except for the start of the incubation of samples made with a 2.0 and 1.6 M PA concentration.

Using the weight loss measurements and assuming that all PA reacted with β-TCP during setting, the DCP and DCPD weight fractions could be calculated (Fig. 5). The DCP weight fraction increased with an increase in the PA concentration (Fig. 5a). The fractions were close to 50, 20 and 10% at PA concentrations of 2.4, 2.0 and 1.6 M, respectively. The fractions were larger in samples dried directly after setting and made with PA concentrations of 2.0 and 1.6 M. The DCPD weight fractions were close to 50% at a PA concentration of 2.4 M and around 70% at PA concentrations of 1.6 and 2.0 M (Fig. 5b). As follows, the β-TCP weight fraction was close to 0, 10 and 20% at PA concentrations of 2.4, 2.0 and 1.6 M, respectively.

The XRD spectra indicated the presence of DCP in all samples prepared with PA 2.4, 2.0 and 1.6 M (Figs 6–8). The DCP peak intensities of the samples prepared with PA 2.4 M were much higher than those prepared with PA 2.0 and 1.6 M. No significant crystallographic differences were observed between samples aged for 6 or 384 h (16 days) at all pHs and temperatures. However, larger DCP diffraction peaks were recorded at 0 h of incubation for cements made with PA 1.6 and 2.0 M.

3.2. Effect of aging temperature

In all experiments done at 23, 37, 40, 45, 50 and 60 °C, equilibrium pH values were in the range 3.7–4.1 (Figs 3 and 9). Small discrepancies could be observed between different series of experiments even though their composition was supposed to be the same. The pH values measured in the first series of experiments (Fig. 3) were consistently lower than those measured in the second (37, 40 and 45 °C) and third (50, 60 and 70 °C) series of experiments. Initially, the pH values measured for samples aged at 70 °C were almost identical to those measured for samples aged at lower temperatures. However, after more than one day of aging, the pH values dropped significantly from 3.8 to 3.5 (Fig. 9). Simultaneously, the samples became very soft. A similar behavior was observed at 60 °C and 384 h aging (16 days). The pH values tended to decrease with an increase of incubating temperature (Figs 3 and 9), but as the measurements were done in three series, it is not possible to know how significant this phenomenon is.

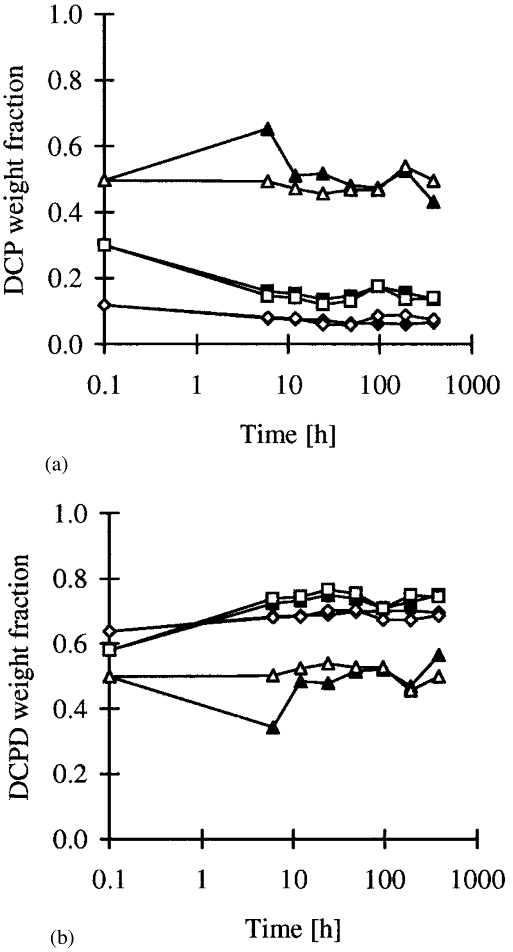

Figure 5 (a) DCP and (b) DCPD weight fraction in the cement as a function of incubation time. The difference between unity and the total of the DCP and DCPD weight fractions corresponds to the β-TCP weight fraction The results given for the time "0.1 h" correspond to the samples dried without previous incubation. Composition of the cement samples: 1.5 g β-TCP and 2 ml H_3PO_4 solution. Temperature and H_3PO_4 concentration: (◆) 23 °C, 1.6 M; (◇) 37 °C, 1.6 M; (■) 23 °C, 2.0 M; (□) 37 °C, 2.0 M; (▲) 23 °C, 2.4 M; (△) 37 °C, 2.4 M.

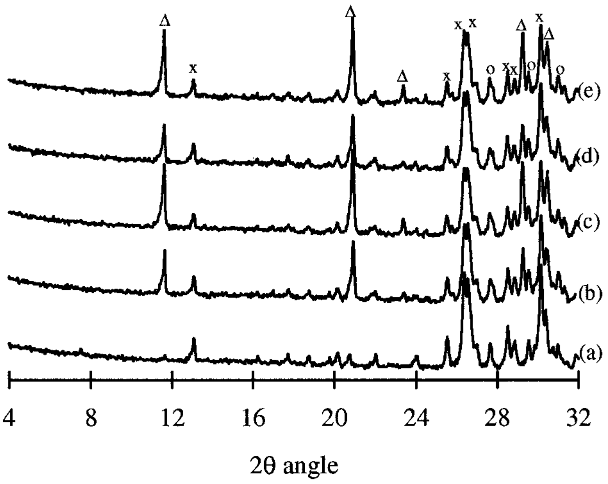

Figure 6 XRD spectra. The cement samples are made of 1.5 g β-TCP and 2 ml H_3PO_4 2.4 M. Temperature and aging time: (a) 23 °C, 0 h; (b) 23 °C, 6 h; (c) 23 °C, 384 h; (d) 37 °C, 6 h; (e) 37 °C, 384 h. (x) main DCP peaks (JCPDS file 9-80); (o) main β-TCP peaks (JCPDS file 9-169); (Δ) main DCPD peaks (JCPDS file 9-77). The diffraction intensity is given in (counts s^{-1})$^{1/2}$.

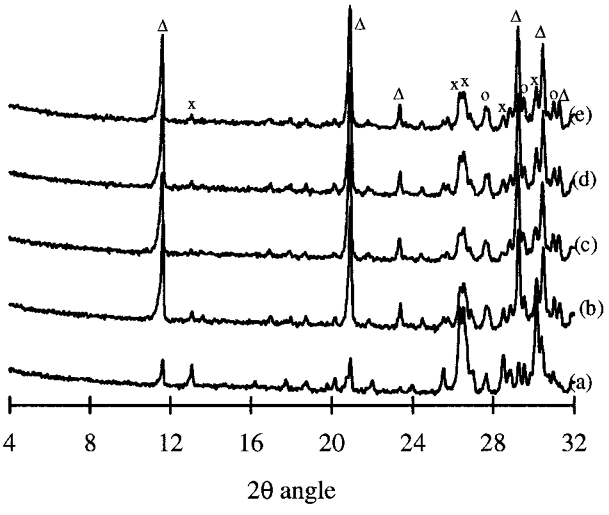

Figure 7 XRD spectra. The cement samples are made of 1.5 g β-TCP and 2 ml H_3PO_4 2.0 M. Temperature and aging time: (a) 23 °C, 0 h; (b) 23 °C, 6 h; (c) 23 °C, 384 h; (d) 37 °C, 6 h; (e) 37 °C, 384 h. (x) main DCP peaks (JCPDS file 9-80); (o) main β-TCP peaks (JCPDS file 9-169); (Δ) main DCPD peaks (JCPDS file 9-77). The diffraction intensity is given in (counts s^{-1})$^{1/2}$.

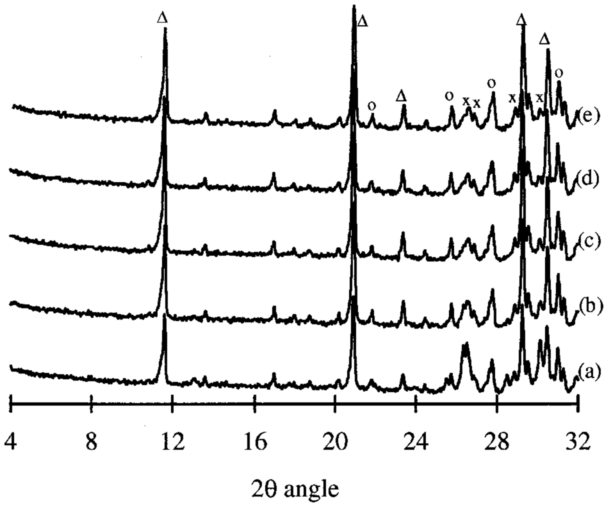

Figure 8 XRD spectra. The cement samples are made of 1.5 g β-TCP and 2 ml H_3PO_4 1.6 M. Temperature and aging time: (a) 23 °C, 0 h; (b) 23 °C, 6 h; (c) 23 °C, 384 h; (d) 37 °C, 6 h; (e) 37 °C, 384 h. (x) main DCP peaks (JCPDS file 9-80); (o) main β-TCP peaks (JCPDS file 9-169); (Δ) main DCPD peaks (JCPDS file 9-77). The diffraction intensity is given in (counts $s^{-1})^{1/2}$.

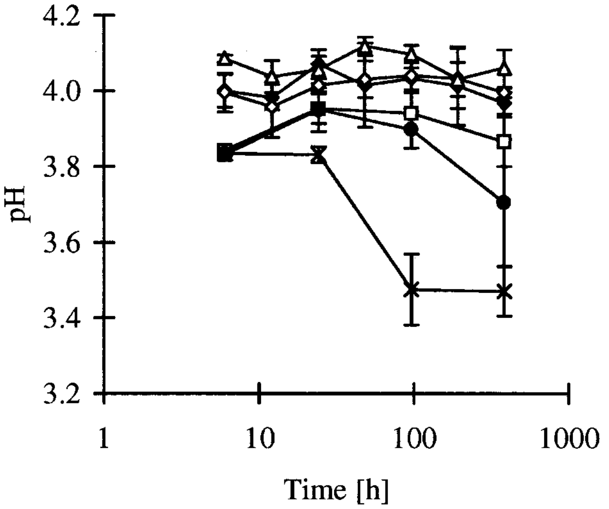

Figure 9 pH of the incubation solution after different times and at different temperatures: (Δ) 37 °C; (◆) 40 °C; (◇) 45 °C; (□) 50 °C; (●) 60 °C; (×) 70 °C. Composition of the cement samples: 1.5 g β-TCP and 2 ml H_3PO_4 2 M. The error bars correspond to the 95% confidence interval on the mean.

The cement specimens aged at different temperatures contained mostly DCPD crystals and only a small amount of DCP crystals (Fig. 10). In the samples aged at 60 °C for 384 h (16 days) and at 70 °C for 24, 92 and 384 h, no DCPD crystals were observed. The samples consisted mainly of DCP crystals. For the latter series of samples, the weight losses were close to 6% (Fig. 11), which is close to the value expected if all DCPD initially present in the cement sample was transformed into DCP. For all other specimens, the weight losses were close to 21%.

4. Discussion

The pH decrease of the aging solution measured when a higher PA concentration was used is due to the higher acidity of the cement paste (Figs 2 and 3) as previously evidenced [11]. The lower pH measured at a higher aging

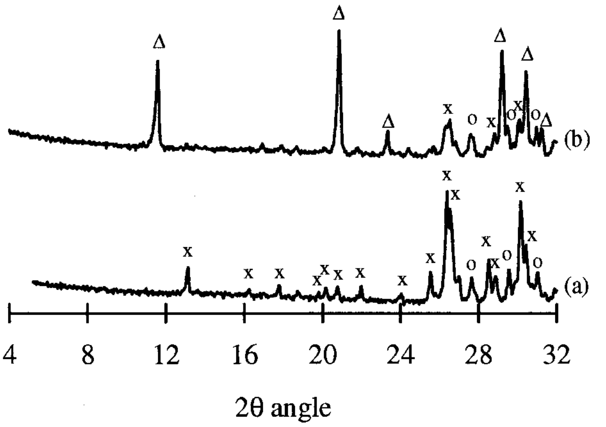

Figure 10 XRD spectra of cements aged for 384 h (16 days) at (a) 23 °C and (b) 70 °C. Composition of the cement samples: 1.5 g β-TCP and 2 ml H_3PO_4 2 M. (x) main DCP peaks (JCPDS file 9-80); (o) main β-TCP peaks (JCPDS file 9-169); (Δ) main DCPD peaks (JCPDS file 9-77). The diffraction intensity is given in (counts $s^{-1})^{1/2}$.

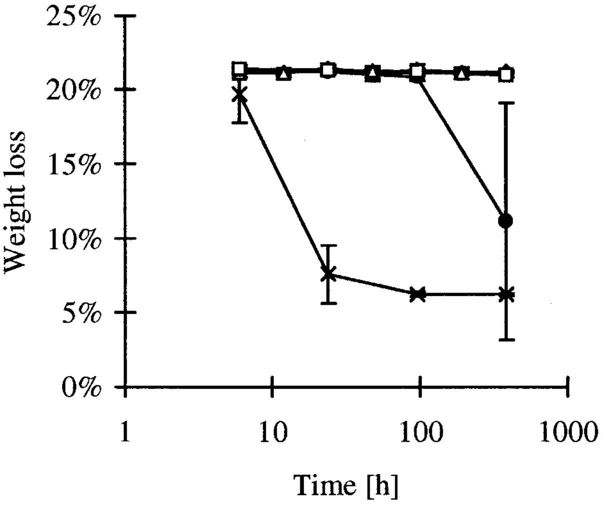

Figure 11 Weight loss of the cement specimens as a function of incubation time and temperature: (Δ) 37 °C; (◆) 40 °C; (◇) 45 °C; (□) 50 °C; (●) 60 °C; (x) 70 °C. Composition of the cement samples: 1.5 g β-TCP and 2 ml H_3PO_4 2 M. The error bars correspond to the 95% confidence interval on the mean.

temperature (Figs 3 and 9) is due to a change of the equilibrium pH between DCPD (or DCP) and β-TCP. As the solubility of DCPD, DCP and β-TCP decreases with an increase of temperature (Table I), a decrease of the equilibrium pH should be measured. When DCPD transforms into DCP, an increase of the equilibrium pH would be expected as the equilibrium pH between DCP

TABLE I Standard free energy, $\Delta G°$, for the dissolution reaction of DCP [15], DCPD [14] and β-TCP [20]. Dissolution reactions: DCP: $CaHPO_4 = Ca^{2+} + HPO_4^{2-}$; DCPD: $CaHPO_4 \cdot 2H_2O = Ca^{2+} + HPO_4^{2-} + 2H_2O$; β-TCP: $\beta - Ca_3(PO_4)_2 = 3Ca^{2+} + 2PO_4^{3-}$. Parabolic least square fitting: $\Delta G°$(DCP) (kJ mol^{-1}): $0.0005 \times T^2 + 0.1663 \times T + 34.828$; $\Delta G°$(DCPD) (kJ mol): $0.0008 \times T^2 + 0.0909 \times T + 34.832$. $\Delta G°$(DCP) = $\Delta G°$(DCPD) when $T = 0.05$°C

	Temperature, T (°C)			
$\Delta G°$ (kJ mol^{-1})	5	15	25	37.5
DCP	35.7	37.4	39.4	41.8
DCPD	35.3	36.4	37.6	39.4
β-TCP	36.9	37.9	39.4	41.9

and β-TCP is higher than that between DCPD and β-TCP [20] (Fig. 2). Paradoxically, a pH decrease is observed (Fig. 9), as if the cement had an excess of PA instead of an excess of β-TCP (Fig. 2). The equilibrium pH values are indeed very low compared with the expected value (5.9). Moreover, the experimental pH decrease (approximately 0.3) is close to that predicted for the transformation of DCPD into DCP in the presence of an excess of PA (approximately 0.2). Therefore, the results suggest that the equilibrium solution does not see the β-TCP particles remaining in the cement samples after setting. One explanation could be that the TCP crystals are covered with a layer of DCP or DCPD crystals during setting, hence stopping prematurely the setting reaction and leading to low pH values. This could in particular explain why, with the same cement composition (1.5 g β-TCP, 2.0 ml PA 2.0 M), a decrease of the β-TCP specific surface area leads to a decrease of the equilibrium pH of the incubation solution (unpublished results).

Assuming that the β-TCP crystals are totally covered by DCP or DCPD crystals, the pH decrease occurring during the transformation of DCPD into DCP can be expressed in simple terms by

$$Ca^{2+} + H_2PO_4^- \rightarrow CaHPO_4 + H^+ \qquad (6)$$

$H_2PO_4^-$ ions are the most abundant orthophosphate ions at pH 4. Moreover, as DCP is less soluble than DCPD (Fig. 1), some of the ions present in the aging solution must precipitate during the transformation of DCPD into DCP, hence leading to the observed pH drop.

The weight loss measurements (Fig. 4) are explained by the occurrence of DCPD and DCP in the cement samples (Figs 6–8). With PA 1.6 M, most β-TCP was transformed into DCPD (Fig. 8). Moreover, there was hardly any DCP in the cement samples (Figs 5a and 8). However, the stoichiometric PA concentration according to Equation 3 is close to 2.4 M. Therefore, 30% of the initial β-TCP amount was still present and the absolute DCPD amount was moderately high (Fig. 5b), resulting in a moderately high weight loss (approximately 18%). With PA 2.0 M, the DCP weight fraction was higher than with PA 1.6 M as evidenced by the weight loss analysis (Fig. 5a) and XRD analysis (Figs 7 and 8). Moreover, the absolute DCPD amount was also slightly larger (Fig. 5b). The increase in DCP and DCPD weight fractions is compensated by the decrease of the β-TCP weight fraction, as evidenced by the decrease of the relative intensity of the β-TCP peak (Figs 7 and 8). Therefore, a higher weight loss was measured (Fig. 4). With PA 2.4 M, there was still a rather large peak at 31.06° 2θ corresponding to the largest diffraction peak of β-TCP (JCPDS File 9-169), but this peak could also be due to a small DCP peak (8% DCP peak according to JCPDS File 9-80) (Fig. 6). Therefore, almost all β-TCP had probably reacted and been transformed into DCPD and DCP (Figs 5 and 6). Due to the much lower DCPD weight fraction in the cement paste, the weight loss of cements made with PA 2.4 M was lower than that of cements made with PA 2.0 M (Fig. 5b).

A temperature of 60 °C has been reported to be an important temperature for the formation of DCP crystals. For example, kinetics are meant to favor the formation of DCPD below 60 °C [10]. Moreover, Frêche and Heughebaert [16] could only grow DCP crystals above 60 °C. Our present results confirm that 60 °C is an important temperature as DCPD crystals start decomposing beyond this temperature (Figs 9–11). They also confirm that temperature has a strong effect on DCPD decomposition. For example, at 60 °C the transformation of DCPD into DCP started after 16 days of aging whereas at 70 °C, all DCPD had been transformed within one day. However, considering the thermal stability of DCPD crystals in the cement paste, it is puzzling to see how much DCP is formed during setting (Figs 6–8).

Fulmer and Brown [17] proposed that in certain conditions, DCP could precipitate directly from a solution at temperatures below 60 °C. They studied the effects of temperature on the formation of hydroxyapatite via MCPM–TetCP–water mixtures. At a temperature below 45 °C, DCPD, TetCP and HA were found in the cement samples reacted for 4 h. At 45 °C, DCP, DCPD, TetCP and HA were observed. At 60 °C, the samples contained only DCP, TetCP and HA. The authors proposed two mechanisms for the formation of DCP: (i) DCPD transforms into DCP, and (ii) there is a simultaneous formation of DCPD and DCP. To check these mechanisms, the authors determined the compositional changes during setting at 45 °C. The setting reaction was stopped by quenching the cement paste in acetone after 15 and 30 s and 1, 2, 5, 10, 15, 20, 30 and 60 min. The XRD patterns showed that DCPD and DCP were both present during the first hour of reaction, indicating that both formed simultaneously. However, quenching the cement paste in acetone must have precipitated the calcium and orthophosphate species present in the mixing liquid. It is therefore possible that this quenching led to an artefact, i.e. to the precipitation of DCP crystals. The latter phenomenon was, for example, observed when a cement paste made of β-TCP–PA–water mixtures was quenched in ethanol [6]. If DCP could precipitate directly from a solution, its precipitation conditions would be very restrained, because most studies report that DCP is formed from DCPD crystals (for example, [9, 12, 16]). Furthermore, there is to our knowledge no evidence of the direct precipitation of DCP crystals from an aqueous solution at room temperature and atmospheric pressure. We therefore believe that DCP crystals result from the recrystallization of DCPD crystals, but that the latter reaction is very slow except at a low pH and a high temperature. This would in particular explain why DCP and DCPD crystals can coexist for several weeks at a temperature inferior to 60 °C and at a moderate pH (Figs 9–11) whereas DCPD can readily convert to DCP below 37 °C at low pH [10].

The increased DCP amounts found in samples prepared with an increased PA concentration result probably from the low pH occurring in the cement paste during setting [11]. A higher PA concentration shifts the pH profile to lower pH values. Thus, a higher DCP amount is expected to form at a higher PA concentration. The heat exhausted during setting could also favor DCP formation. Just after setting, the outer surface of the cement samples was warm, close to 40 °C.

Inside the cement sample, the temperature can thus be expected to reach even higher values. As a low pH and a high temperature trigger the transformation of DCPD into DCP, large DCP amounts could be easily produced during setting.

Surprisingly, the absence of incubation of specimens made with PA concentrations of 1.6 and 2.0 M increased the DCP weight fraction (Fig. 5). Assuming that a low pH and a high temperature trigger the transformation of DCPD into DCP, two explanations could account for this phenomenon: (i) the setting reaction was prematurely stopped by drying, thus leading to a lower internal pH of the cement specimen and hence to a higher DCP amount; (ii) the temperature of the cement samples was reduced by the addition of the aging liquid, hence decreasing the amount of DCP formed during setting.

5. Conclusions

This study has confirmed that a low pH and a high temperature trigger the decomposition of DCPD into DCP. When the initial PA concentration of β-TCP–PA–water cements increased, the equilibrium pH of the incubating solution decreased and the amount of DCP increased. For example, there was ten times less DCP than DCPD at a PA concentration of 1.6 M, whereas at a PA concentration of 2.4 M, there was as much DCP as DCPD. However, the results showed that the cement composition was very stable over time, as long as the incubation temperature was kept below 60 °C. At 60 °C, DCPD started decomposing after 16 days of aging. At 70 °C, DCPD was totally replaced by DCP within the first day. The latter reaction provoked a decrease of the pH of the incubating solution. This decrease could only be explained if the sample contained an excess of PA. As it was not the case in the initial composition, it was postulated that the β-TCP particles were covered with DCPD or DCP crystals during setting, hence stopping the setting reaction before completion.

Appendix

The equilibrium pH of a volume, *V*, of deionized water put in contact with a mass, *m*, of cement containing an excess of PA can be determined from the initial cement composition and solubility data. The detail of the calculation is given hereafter for DCPD. The same method applies for anhydrous dicalcium phosphate ($CaHPO_4$; DCP). In this appendix, it is assumed that the hardened cement sample contains only DCPD when prepared with an excess of PA. According to LeChatelier, the amount of calcium and phosphate ions remains constant before and after reaction

$$n_{\mathrm{Ca,TCP}} = n_{\mathrm{Ca,DCPD}} + n_{\mathrm{Ca,sol}} \tag{A1}$$

$$n_{\mathrm{P,PA}} + n_{\mathrm{P,TCP}} = n_{\mathrm{P,DCPD}} + n_{\mathrm{P,sol}} \tag{A2}$$

where n_{Ca} and n_{P} are the molar amounts of Ca and P in PA, β-TCP, DCPD and the solution. Knowing the cement composition, the left terms of Equation A1 and A2 are known. Also, by definition

$$n_{\mathrm{Ca,DCPD}} = n_{\mathrm{P,DCPD}} \tag{A3}$$

The incubation solution must be in equilibrium with the cement. In other words, the amount of Ca and P in the solution is related to the solubility isotherm of DCPD according to

$$n_{\mathrm{Ca,sol}} = [\mathrm{Ca}]_{\mathrm{tot}} \times V \tag{A4}$$

$$n_{\mathrm{P,sol}} = [\mathrm{P}]_{\mathrm{tot}} \times V \tag{A5}$$

where $[\mathrm{Ca}]_{\mathrm{tot}}$ and $[\mathrm{P}]_{\mathrm{tot}}$ are the total concentrations of Ca and P dissolved in the solution. Both concentrations depend on the pH according to the DCPD adsorption isotherm [14]

$$[\mathrm{Ca}]_{\mathrm{tot}} = f(\mathrm{pH}) \tag{A6}$$

$$[\mathrm{P}]_{\mathrm{tot}} = g(\mathrm{pH}) \tag{A7}$$

Using Equations A1–A7, the seven unknowns $(n_{\mathrm{Ca,DCPD}}, n_{\mathrm{P,DCPD}}, n_{\mathrm{Ca,sol}}, n_{\mathrm{P,sol}}, [\mathrm{Ca}]_{\mathrm{tot}}, [\mathrm{P}]_{\mathrm{tot}}, \mathrm{pH})$ can be easily determined, in particular, the pH corresponding to the starting cement composition.

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