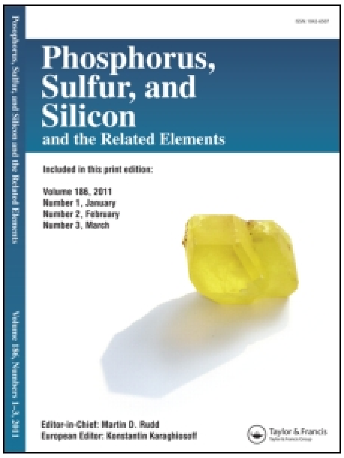

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Formation of Hydroxyapatite in Cement Systems: Effects of Phosphate

LAURENCE C. CHOW, MILENKO MARKOVIC and
SHOZO TAKAGI

*Paffenbarger Research Center, American Dental Association Health Foundation,
National Institute of Standards and Technology, Gaithersburg, MD 20899, U.S.A.*

The rate of hydroxyapatite (HA) formation in several calcium phosphate cement (CPC) systems was promoted when a phosphate solution instead of water was used as the cement liquid. The accelerated HA formation reduced the hardening time (HT) of the cements. In the cement system consisting of tetracalcium phosphate (TTCP), dicalcium phosphate anhydrous (DCPA), and distilled water, the presence of small TTCP particles (median diameter of 2.7 μm) reduced phosphate concentration in liquid phase, inhibited HA formation, and prolonged HT.

Keywords: calcium phosphate cements; diametral tensile strength; hardening time; hydroxyapatite; phosphate ions

INTRODUCTION

Previous studies showed that the composition and particle sizes of powdered calcium phosphate cement (CPC) components together with the cement liquid composition are the major parameters that control the cement hardening process[1-5]. Tetracalcium phosphate (TTCP), because of its high reactivity, was found to be a necessary component of CPC when water was used as the cement liquid. When a phosphate solution was used as the cement liquid, numerous CPC mixtures that do not contain TTCP can also harden fast[6-8]. In this paper the relationship between phosphate concentration, hydroxyapatite (HA) formation, and hardening time (HT) in different cement systems was investigated.

MATERIALS AND METHODS

The particle size distribution and median particle diameter (MD) of the ball-milled TTCP, α-tricalcium phosphate (α-TCP), dicalcium phosphate anhydrous (DCPA), and calcium carbonate ($CaCO_3$) powders were determined with a centrifugal particle size analyzer (SA-CP3, Shimadzu). Three two-component CPC mixtures with a Ca/P molar ratio of 1.67 were prepared: (I) α-TCP + $CaCO_3$, (II) DCPA + $CaCO_3$, and (III) TTCP + DCPA. Cement pastes, prepared by mixing 0.3 g of the CPC powder with adequate volume of cement liquid (distilled water or 0.5 mol/L Na_2HPO_4 solution), were packed into stainless steel moulds (diameter 6 mm and height 3 mm) with a manually applied pressure of 1 MPa to 1.5 MPa. The samples were kept in 100 % relative humidity at 37 °C and tested for hardening time (HT) with the use of a Gillmore needle that has a mass of 0.4536 kg (1 lb) and a point of 1.0583 mm (1/24 inch) in diameter.

X-ray diffraction (XRD) patterns of the cement samples were determined by Rigaku DMAX-2200 diffractometer.

The loading forces necessary to crack the wet CPC pellets, that were aged for 4 h in 100 % relative humidity and 20 h in distilled water, were measured by an Instron instrument. Diametral tensile strength (DTS) of 24 h aged pellets, expressed in megapascals (MPa), was calculated from the equation, DTS = $2F/\pi DH$, where F is loading force in newtons (N) and D and H are diameter and height of the pellet in millimeters (mm), respectively.

MD, HT, and DTS determined for replicate samples (n) are expressed as the mean value ± standard uncertainty.

RESULTS AND DISCUSSION

(I) α-TCP + $CaCO_3$ cement system

A mixture consisting of α-TCP (MD 5.0 μm ± 1.3 μm, n = 3) and $CaCO_3$ (MD 3.5 μm ± 0.8 μm, n = 3) was combined with distilled water (cement system I-w) or 0.5 mol/L Na_2HPO_4 solution (cement system I-p). The powder-to-liquid ratio (P/L) was 3 g/mL. A dramatic reduction in HT (from ~ 3 h in I-w versus ~ 8 min in I-p) was observed when the phosphate solution instead of distilled water was used as the cement liquid (Table I). The difference in DTS mean values for I-w and I-p cements was not statistically significant.

TABLE I Hardening times (HT) and diametral tensile strengths (DTS) for α-TCP + $CaCO_3$ cement systems (I-w and I-p) with different cement liquids

Cement liquid	HT (min)	DTS (MPa)
(I-w) Distilled water	192 ± 16 (n = 4)	5.9 ± 1.5 (n = 4)
(I-p) 0.5 mol/L Na_2HPO_4	8.2 ± 0.3 (n = 5)	6.2 ± 1.3 (n = 11)

Figure 1 shows the XRD patterns of the initial α-TCP + $CaCO_3$ powdered mixture and of the cement samples hardened in distilled water (cement system I-w) or 0.5 mol/L Na_2HPO_4 solution (cement system I-p) determined in reaction times of 1h and 24 h. The formation of HA proceeded with time which was indicated by the increase in intensity of the HA reflections at 2θ = 25.9 °, 31.8 °, 32.2 °, and 32.9 ° (marked with asterisks in Figure 1). Initially (inside 1 h of reaction), the formation of HA in the cement system with phosphate solution as the cement liquid (I-p) was significantly faster compared to the cement system in which water was used as the cement liquid (I-w). After 24 h, the conversion of cement components to poorly crystalline HA was nearly complete in both I-w and I-p cement systems, but the amounts of unreacted cement components were higher in the cement system I-w.

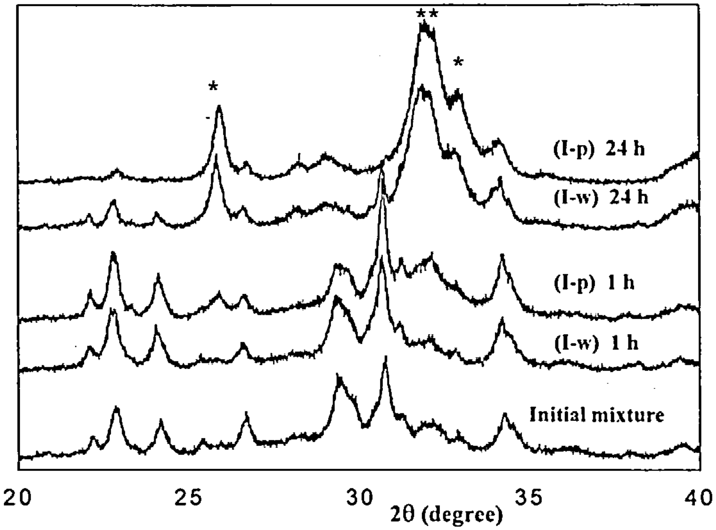

FIGURE 1 XRD patterns of α-TCP + $CaCO_3$ cement system: initial cement mixture and cement products after 1 h and 24 h reaction in distilled water (I-w) or 0.5 mol/L Na_2HPO_4 solution (I-p). Hydroxyapatite peaks are marked with asterisks.

(II) DCPA + $CaCO_3$ cement system

A mixture consisting of DCPA (MD 1.0 μm ± 0.1 μm, n = 7) and $CaCO_3$ (MD 3.5 μm ± 0.8 μm, n = 3) was mixed with water (cement system II-w) or 0.5 mol/L Na_2HPO_4 solution (cement system II-p) at P/L of 3 g/mL. A significant reduction in HT (~ 3 h in II-w versus 24 min in II-p) was observed when the phosphate solution was used as the cement liquid (Table II). The content of poorly crystalline HA increased faster when the phosphate solution was used. After 24 h, the amounts of unreacted initial components in systems II-w and II-p were higher than in the α-TCP + $CaCO_3$ systems I-w and I-p.

Table II Hardening times (HT) and diametral tensile strengths (DTS) for DCPA + $CaCO_3$ cements with different cement liquids

Cement liquid	HT (min)	DTS (MPa)
(II-w) Distilled water	196 ± 13 (n = 4)	1.6 ± 0.4 (n = 4)
(II-p) 0.5 mol/L Na_2HPO_4	24 ± 2 (n = 4)	2.1 ± 0.4 (n = 6)

(III) TTCP + DCPA cement system

Two mixtures of TTCP + DCPA (III-a and III-b) that contained DCPA particles with MD of 1.1 μm ± 0.1 μm, n = 6, and (III-a) large TTCP particles with MD of 16.2 μm ± 1.4 μm, n = 6, or (III-b) small TTCP particles with MD of 2.7 μm ± 0.5 μm, n = 3, were prepared. For both mixtures water was the cement liquid and P/L was 4 g/mL. Mixture III-a hardened in 30 min and mixture III-b hardened in > 3 h.

To determine the composition of the cement liquids in the TTCP + DCPA cement systems, slurries that contained mixture III-a or III-b and water with a P/L of 0.4 g/mL (ten times lower than in the cement pastes) were prepared. The pHs and phosphate concentrations in the liquid phases were determined after 3 min and 15 min of reaction. After 3 min of reaction, the phosphate concentration in solution III-b was about ten times lower than that in solution III-a, and after 15 min the phosphate concentration in solution III-b was about three times lower. The pH in solution III-b was about one unit lower than that in solution III-a at both 3 min and 15 min. These data indicated that the presence of small TTCP particles caused a drastic decrease in the phosphate concentration and this may be the cause for the prolonged HT.

TABLE III Phosphate concentrations and pHs in TTCP + DCPA cement system (P/L = 0.4 g/mL, cement liquid is distilled water) with large (III-a) and small (III-b) TTCP particles

Cement system	$[PO_4]$ (mmol/L)		pH	
	3 min	15 min	3 min	15 min
(III-a) TTCP (16.2 μm) + DCPA (1.1 μm)	0.30	0.26	7.8	8.1
(III-b) TTCP (2.7 μm) + DCPA (1.1 μm)	0.03	0.09	8.7	8.8

CONCLUSIONS

A sufficiently high level of phosphate ions in the cement liquid of CPC is crucial for HA formation and rapid cement hardening.

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Certain commercial materials and equipment are identified in this paper to specify the experimental procedure. In no instance does such identification imply recommendation or endorsement by the American Dental Association Health Foundation or the National Institute of Standards and Technology or that material or equipment identified is necessarily the best available for the purpose.

References

[1] Y. Fukase, E. D. Eanes, S. Takagi, L. C. Chow, and W.E. Brown, *J. Dent. Res.* **69**, 852 (1990).

[2] K. Ishikawa, S. Takagi, L. C. Chow, and Y. Ishikawa, *J. Mater. Sci.: Mater. Med.* **6**, 528 (1995).

[3] L. C. Chow, M. Markovic, S. Takagi, and M. Cherng, *Innov. Techn. Biol. Med.* **18**, 11 (1997).

[4] M. Markovic, S. Takagi, D. Kim, and L. C. Chow, *J. Dent Res.* **76**, 381 (1997).

[5] S. Takagi. M. Markovic, and L.C. Chow, *J. Dent Res.* **77**, 848 (1998).

[6] M. Markovic, S. Takagi, and L.C. Chow, *J. Dent Res.* **75**, 25 (1996).

[7] M. P. Ginebra, M. G. Boltong, E. Fernandez, J. A. Planell, and F. C. M. Driessens, *J. Mater. Sci.: Mater. Med.* **6**, 612 (1995).

[8] S. Takagi, L.C. Chow, and K. Ishikawa, *Biomaterials* **19**, 1593 (1998).