A Rapid Setting TTCP-DCPD Cement. Study of the Setting Reaction as a Function of Time

E.F. Burguera^{1,a}, F. Guitián^{2,b} and L.C. Chow^{1,c}

¹Paffenbarger Research Center, ADAF at NIST, Gaithersburg, MD 20899, USA

²Instituto de Cerámica de Galicia, Universidad de Santiago de Compostela, Santiago de Compostela 15786, Spain

^aelena.burguera@nist.gov, ^bcekiko@usc.es, ^clarry.chow@nist.gov

Keywords: Calcium phosphate cement, dicalcium phosphate dihydrate, tetracalcium phosphate, hydroxyapatite formation, compressive strength, setting reaction.

Abstract. The progression of the setting reaction of a tetracalcium phosphate (TTCP) –dicalcium phosphate dihydrate (DCPD) rapid setting cement was investigated as a function of time. Compressive strength and extent of conversion to hydroxyapatite (HA) were obtained at different incubation times. The results indicated a rapid development of both strength and HA conversion in the early stages of the reaction, which slowed down after 4 h, presumably as a result of HA formation on the surface of the reactants. This hypothesis was supported by scanning electron microscopy examination of cement fracture surfaces.

Introduction: Calcium phosphate cements are promising materials as bone graft substitutes. Presently, research is focused on developing strong, fast-setting and fast-resorbed materials. Several formulations have been tested that set in a very short time (i.e. ≈ 10 min) with the use of setting accelerators such as organic acids or phosphate-containing solutions, but setting times (ST) with water are usually much longer. Previous studies from our laboratory showed that a tetracalcium phosphate (TTCP)-dicalcium phosphate dihydrate (DCPD) cement can set in (14 ± 1) min with water by choosing appropriately synthesized cement components [1]. Results showed that the cement components were not fully reacted at 24 h. In this study, the cement setting reaction was stopped at specified time periods and the resulting samples were characterized to provide more complete information about the progression of the setting reaction with time.

Materials and methods:

Cement preparation. Calcium phosphate cement (CPC) mixtures were prepared by thoroughly blending equimolar amounts of TTCP and DCPD. TTCP was prepared by heating a mixture of dicalcium phosphate anhydrous (DCPA) and calcium carbonate at 1500 °C for 6 h in a furnace, followed by quenching at room temperature. The Ca/P molar ratio in the TTCP was 1.90 to avoid the presence of CaO, known to adversely affect the cement. X-ray diffraction analysis showed that the product was predominantly TTCP with a minor amount of α -tricalcium phosphate also present. The TTCP was dry-ground in a ball mill to obtain a median particle size of $(17 \pm 1) \mu m$. DCPD was synthesized in the laboratory by slowly raising the pH (by means of adding CaCO₃) of a 1.9, DCPD-monocalcium phosphate monohydrate singular point solution at 4 °C. CaCO₃ was used to raise the pH because by continuously supplying a calcium source to the solution, the yield of the synthesis can be greatly increased. The synthesized DCPD was ground in water in a ball mill to obtain a median particle size of $(1.7 \pm 0.3) \mu m$. Distilled water or a dilute sodium phosphate solution (0.25 mol/L, pH = 6.3) was used as the setting liquid. This phosphate solution was prepared by diluting a commercially available sodium phosphate solution.

Measurements of sample compressive strength (CS) as a function of time. Samples for CS measurements were prepared by mixing CPC powder and the setting liquid at a powder to liquid ratio of 4. The resulting paste was placed in a stainless steel mold (6 mm in diameter), that was



then placed in a constant-pressure loading device described previously [2], and allowed to set in the molds for 30 min at 37 °C and 100 % relative humidity. The samples were then removed from the molds, immersed in 3 ml of distilled water for variable time periods so that total hardening time was (0.5, 1, 2, 4, 8 or 24) h. CS measurements were performed on wet specimens after the prescribed incubation time using a computer-controlled Universal Testing Machine (Instron, United Calibration Corp., Garden Grove, CA)^{*} at a loading rate of 1 mm/min. Based on standard deviation (n = 6) of the data obtained in the present study, the estimated standard uncertainty of CS measurement was about 10 %. The dimensions of each cement specimen were measured with a micrometer. After the CS measurement, the broken pieces of each specimen were collected, immersed in ethanol and dried at 70 °C. Density values were calculated with the obtained dry masses and the specimen dimensions.

Estimation of the extent of cement setting reaction as a function of time by powder X-ray diffraction (XRD) analysis. To study the progression of the setting reaction as a function of time, another set of CPC samples was prepared following the procedure described above and after the prescribed incubation periods, the specimens were crushed with mortar and pestle, thoroughly washed with acetone and air dried. This procedure stopped the progression of the setting reaction by eliminating water needed for the reaction. XRD analysis (Rigaku, Danvers, MA, USA) was used to estimate the extent of CPC conversion to HA for each CPC mixture. Scans were performed between $10^{\circ} < 20 < 50^{\circ}$ at 1 °/min. Three scans were performed for each incubation period. The relative peak intensities of the DCPD peaks located at 11.68° and 20.93° were measured and averaged. These peaks were selected because they are free of overlapping. The estimated standard uncertainty in 20 measurements was 0.01° and the minimun mass fraction of a calcium phosphate phase that can be detected by XRD is about 3 %. The extent of the cement setting reaction was estimated from the DCPD intensity data using Eq. 1, derived from Fukase et al. [3]

$$EC_{DCPD} = \frac{D_0 - D_t}{D_0 - D_{24}} \cdot 100$$
(1)

where, EC_{DCPD} is the extent of conversion in terms of DCPD consumption, and D_0 , D_{24} and D_t are the sum of the intensities of the DCPD peaks at 11.68° and 20.93° at time zero (unreacted mixture), 24 h (sample prepared with distilled water as the setting liquid) and time t (distilled water or phosphate solution as the setting liquid), respectively. The 24 h samples prepared with water as the setting liquid showed the highest mean conversion; this mean was considered to be the maximum extent of conversion attainable in 24 h and was assigned an arbitrary value of 100 % conversion. The rest of the samples, prepared with water or phosphate solution were compared with this value.

Examinations of sample morphology by scanning electron microscopy (SEM). SEM was used to evaluate the morphology of fracture surfaces of the 24 h set cement specimens. Set cement specimens were sputtered with gold prior to SEM examination (JEOL, JSM-5300, JEOL USA Inc., Peabody, MA, USA).

Statistical analysis. Two-way analysis of variance (ANOVA) was performed on compressive strength and density with incubation time and setting liquid being the independent variables. Newman-Keuls multiple comparison tests were conducted if a significant difference (p < 0.05) existed.

^{*} Certain commercial equipment, instruments or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the NIST or the ADAF, nor does it imply that the materials or equipment identified are necessary the best available for the purpose



17

the TTCP-DCPD cement specimens subjected to different incubation times. The analyses showed that both incubation time and liquid used had a significant effect (p < 0.001)

on the compressive strength values, and there were significant (p <0.05)interactions between the factors. Increasing the produced incubation time stronger cements, and the use of phosphate produced weaker cements when compared to those prepared with water as the setting liquid.

These results seem to be indicative of a fast development of strength in the early stages of

Incubation	CS, [MPa]		Density, [g/cm ³]	
time [h]	Water	Phosphate	Water	Phosphate
0.5	$24.4{\pm}0.7^1$	21.7 ± 0.5	1.74 ± 0.02	1.74 ± 0.01
1	30.3 ± 1.7	24.1 ± 1.1^2	1.74 ± 0.01	1.74 ± 0.01
2	34.1±1.0	25.5 ± 1.5	1.74 ± 0.02	1.74 ± 0.02
4	36.1 ± 1.8	26.3 ± 1.4	1.74 ± 0.01	1.76 ± 0.03
8	41.9±1.3	26.9 ± 2.7	1.74 ± 0.01	1.73 ± 0.02
24	44.0 ± 2.8	36.5 ± 2.4	1.74 ± 0.01	1.76 ± 0.01

Table 1 – CS and density values of CPC specimens prepared with TTCP-DCPD cement at different incubation times.

¹mean \pm standard deviation, n = 6; ²values connected with a line are not significantly different, p > 0.05

the reaction. It is interesting to note that the cement acquired 24.4 MPa in the first 30 min of reaction, which is more than 50 % of its final strength. The strength development seemed to slow after 2 h as reflected by the fact that 2 h and 4 h values, and 8 h and 24 h values are not different.

When using phosphate solution the strength development in the initial stages was even faster than when using water; even though the 0.5 h CS value is significantly lower than the corresponding water-set value, it accounted for 59 % of the 24 h strength. However, this very fast hardening of the cement also seemed to prevent further strength development at longer times.

Neither the time of incubation nor the setting liquid significantly affected density. Multiple comparisons of marginal means showed that all density values obtained at the different incubation times were not significantly different. This would suggest that final density of any cement sample is defined by the amount of water used and the cement sample preparation procedure, and it is not

significantly modified by the length of the setting reaction. Density was also not affected by the use of phosphate solution instead of distilled water as the setting media, again supporting the hypothesis that density is defined by physical rather than by chemical factors.

Fig. 1 illustrates the percentage of conversion for the different incubation time periods which were calculated using Eq. 1 from the XRD patterns of the different CPC specimens (Fig. 2) as described above. Compressive strength values were also included to show the apparent common trend for the strength development and the conversion to HA.



Fig. 1 – CS values and percentages of conversion of CPC specimens incubated for different time periods.

Also, conversion to HA in samples prepared with the phosphate solution are lower than those obtained with water as the setting liquid.

The results indicate a fast development of both the strength and HA conversion in the early stages of the reaction, which slowed after 4 h. This, together with the presence of residual amounts



of the starting cement ingredients in 24 h samples observed in this study (Fig. 2), is typical of systems where the anhydrous reactants are blocked from the liquid medium by the precipitating phase. This would suggest that the rate of HA formation was initially controlled by the surface areas of the reactants, and subsequently decreased as a result of the precipitation of HA on the surface of the reactants diminishing the effective surface area.



Fig. 2 – XRD patterns of CPC specimens at different incubation times. specimens.

Eventually a point was reached where further reaction became controlled by the diffusion rate of reacting ions through the HA layer. This hypothesis is supported by SEM examinations of the fractured cement surfaces, where HA growth on TTCP particles appeared to block their surfaces, hindering complete dissolution and reaction of TTCP (Fig. 3).

Summary and conclusions: The study of the progression of the setting reaction of the TTCP-DCPD cement system as a function of time revealed that both the strength and the conversion to HA follow a fast development in the early stages of the reaction, which gradually slowed after 4 h. Both strength and conversion were higher when distilled water was used as the setting liquid as compared with dilute sodium phosphate solution, at any given time point. XRD showed the presence of both reactants, TTCP and DCPD, in the 24 h CPC specimen, and SEM provided evidence that TTCP particles become surrounded by precipitating HA, which may explain why the setting reaction did not reach completion in 24 h even when both reactants were available. The results suggest that reductions in median particle sizes of the reactants should delay the onset of the diffusion-controlled stage of the setting reaction and increase the extent of HA formation in the final set cement sample. This work was supported in part by NIH grant DE11789 and MCYT grant MAT 02-03857. E.F. Burguera gratefully acknowledges the Spanish Ministry of Education, Culture and Sport and Great West Life Annuity Insurance Co. for their financial support. **References:**

[1] E.F. Burguera, F. Guitian, L.C. Chow: J. Biomed. Mater. Res. Accepted for publication

- [2] L.C. Chow, S. Hirayama, S. Takagi, E. Parry. J. Biomed. Mater. Res. Vol. 53(2000), p. 511
- [3] Y. Fukase, E.D. Eanes, S. Takagi, L.C. Chow, W.E. Brown. J.Dent. Res. Vol. 69(1990), p. 1852



Bioceramics 17 doi:10.4028/www.scientific.net/KEM.284-286

A Rapid Setting TTCP-DCPD Cement. Study of the Setting Reaction as a Function of Time

doi:10.4028/www.scientific.net/KEM.284-286.15

