
Effect of the calcium to phosphate ratio of tetracalcium phosphate on the properties of calcium phosphate bone cement

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Abstract: Six different tetracalcium phosphate (TTCP) products were synthesized by solid state reaction at high temperature by varying the overall calcium to phosphate ratio of the synthesis mixture. The objective was to evaluate the effect of the calcium to phosphate ratio on a TTCP-dicalcium phosphate dihydrate (DCPD) cement. The resulting six TTCP-DCPD cement mixtures were characterized using X-ray diffraction analysis, scanning electron microscopy, and pH measurements. Setting times and compressive strength (CS) were also measured. Using the TTCP product with a Ca/P ratio of 2.0 resulted in low strength values (25.61 MPa) when distilled water was used as the setting liquid, even though conversion to hydroxyapatite was not prevented, as confirmed by X-ray diffraction. The suspected CaO presence in this TTCP may have affected the cohesiveness of the cement mixture but not

the cement setting reaction, however no direct evidence of CaO presence was found. Lower Ca/P ratio products yielded cements with CS values ranging from 46.7 MPa for Ca/P ratio of 1.90 to 38.32 MPa for Ca/P ratio of 1.85. When a dilute sodium phosphate solution was used as the setting liquid, CS values were 15.3% lower than those obtained with water as the setting liquid. Setting times ranged from 18 to 22 min when water was the cement liquid and from 7 to 8 min when sodium phosphate solution was used, and the calcium to phosphate ratio did not have a marked effect on this property. © 2007 Wiley Periodicals, Inc. *J Biomed Mater Res* 85A: 674–683, 2008

Key words: calcium phosphate cement; tetracalcium phosphate; dicalcium phosphate dihydrate; hydroxyapatite; calcium to phosphate ratio

INTRODUCTION

With approximately one million bone grafts performed each year in the United States to treat osseous defects,¹ the development of successful synthetic bone graft substitutes is one of the current concerns of regenerative medicine. Autologous bone graft is the gold standard for bone substitution but it is restricted by donor availability, whereas allografts pose the risk of rejection and disease transfer. Cal-

cium phosphate compounds are one of the preferred choices as an alternative to bone harvesting.² They can be synthesized in unlimited quantity and, most importantly, they are chemically very similar to the mineral phase of bone.³ Calcium phosphate cements are combinations of calcium phosphate compounds that in the presence of water undergo different dissolution/precipitation reactions that result in the rapid hardening of the cement mass.⁴ These materials are biocompatible, osteoconductive, and in most cases gradually resorbed by bone. They can be molded *in situ*, providing optimal adaptation to the defect site.⁵ Many formulations have been tested and several commercial calcium phosphate cements are available.^{6–8}

Pure tetracalcium phosphate (TTCP; $\text{Ca}_4(\text{PO}_4)_2\text{O}$), with a calcium to phosphate (Ca/P) ratio of 2.0, is the only calcium phosphate that has a Ca/P ratio higher than that of hydroxyapatite (HA; $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) which is 1.67, and therefore it plays a unique role as a calcium phosphate cement component in that only TTCP can be combined with other

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calcium phosphate salts with lower Ca/P ratios to formulate a mixture that has the stoichiometry of HA.⁴ Not surprisingly several cement systems have been formulated that contain TTCP, among them a TTCP-dicalcium phosphate anhydrous (DCPA; CaHPO₄) cement,⁹ a TTCP-monocalcium phosphate monohydrate (MCPM; Ca(H₂PO₄)₂·H₂O)- α -tricalcium phosphate (α -TCP; α -Ca₃(PO₄)₂) cement,¹⁰ and a TTCP-dicalcium phosphate dihydrate (DCPD; CaHPO₄·2H₂O) cement.¹¹ TTCP is an example of calcium phosphate that cannot be precipitated from aqueous solutions and thus, it can only be prepared by a solid state reaction at high temperature.^{12,13}

In previous studies, TTCP was synthesized from a starting mixture with a Ca/P ratio of 1.90 to avoid the presence of CaO in the resulting TTCP.^{14,15} Matsuya et al.¹⁶ and Xie and Monroe¹⁷ both indicated that the presence of this compound in the TTCP product is detrimental to the cement properties, and the necessity of keeping the Ca/P ratio below 2.0 for this purpose. But other than that, there has not been any systematic study on the influence of this parameter on the properties of the resulting calcium phosphate cement.

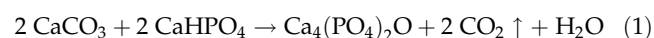
The present study was conducted to investigate the effect of the overall Ca/P ratio of the TTCP synthesis mixture on the properties of the resulting TTCP-DCPD cement.

MATERIALS AND METHODS

Synthesis of TTCP

In this work, TTCP was synthesized following the method described by Brown and Epstein.¹⁸ Reagent grade CaCO₃ (Baker Analytical Reagents, J.T. Baker Chemical Co., NJ) and DCPA, in the appropriate proportions, were thoroughly mixed with water to form a slurry that was left stirring for up to 1 day. This slurry was then filtered and dried, and the cake formed was broken down to powder form. This powder was fired in a high temperature furnace (Keith's FastHeat Furnace EHSK-12, Keith Company, CA) for 6 h at 1500°C in alumina crucibles, followed by rapid quenching at room temperature. Quenching is necessary to avoid the transformation of TTCP to phases that are more stable at lower temperature. The product obtained was dry ground in a blender and then sieved using a standard sieve with openings of 38 μ m to remove large particles.

In these conditions, when the starting CaCO₃-DCPA mixture has an overall Ca/P of 2.0 and homogeneity is achieved, pure TTCP forms according to the following reaction:



In the present work six mixtures with Ca/P ratios between 2.0 and 1.75 were prepared. In those cases when the Ca/P ratio in the starting mixture was lower than 2.0, α -TCP also formed as a secondary phase upon quenching,

according to the following reaction¹²:

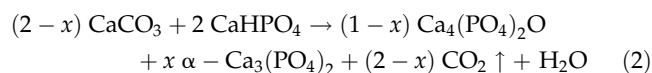


Table I includes a summary of the ratios of reactants used in each synthesis as well as the composition of the resulting products. Strictly speaking, only the pure material, with Ca/P equal to 2.0, should be called TTCP. But to simplify the cement formulation the following notation was adopted: TTCP products are identified with the overall Ca/P ratio of the starting mixture, TTCP_{2.00} through TTCP_{1.75}; therefore TTCP_{1.95} is a mixture of predominantly TTCP and a small amount of a secondary phase, α -TCP according to the proportions in Table I, and so on.

Synthesis of DCPD

DCPD was synthesized using a precipitation method modified from that described by Moreno et al.¹⁹ Accordingly, DCPD was precipitated by slowly raising the pH of a MCPM-DCPD singular point solution with a starting pH of 1.9 and a temperature of 4°C. CaCO₃, instead of NH₄OH was used to increase the pH of the synthesis solution. Changes in pH were continuously monitored by means of a combination pH electrode (Model 60120B, Extech Instruments Corp. MA). The DCPD that precipitated before the pH reached 3.5 (below the HA-DCPD singular point at 4.2) was collected to avoid possible contamination by hydroxyapatite. The precipitated DCPD was washed thoroughly with distilled water and then with ethanol and left to dry in air at room temperature. Drying at higher temperature was avoided to prevent any dehydration of DCPD to DCPA, and once dried the resulting product was kept refrigerated for the same purpose. DCPD was ground in water in a ball mill (Retsch PM4, Brinkman, NY) and the resulting median particle size was (1.7 \pm 0.1) μ m ($n = 2$).

Phase analysis of calcium phosphate powders and cements

Powder X-ray diffraction (XRD) analyses (Rigaku D/max Diffractometer, Rigaku/USA Inc., Danvers, MA) were used to determine phase composition of the different calcium phosphate products synthesized, as well as to confirm the conversion of the different TTCP-DCPD mixtures in the cements to HA. The estimated standard uncertainty in 2 θ measurements was 0.01° and the minimum mass fraction of a calcium phosphate phase that can be detected by XRD is about 3%. Scans were performed between 10° < 2 θ < 50° at 1°/min.

Particle size analysis

Particle size distribution measurements were performed in isopropanol by a sedimentation method based on the Stokes' law using a centrifugal particle size analyzer (SA-CP3, Shimadzu, Kyoto, Japan).

TABLE I
Conditions Used for the Synthesis of TTCP Products With Different Ca/P Ratios

Overall Ca/P	Starting Materials		Theoretical (Expected) Proportions of the Phases in the Products			
	CaCO ₃	DCPA	TTCP		α-TCP	
	Molar Fraction	Molar Fraction	Molar Fraction	Mass Percent	Molar Fraction	Mass Percent
2.0	0.500	0.500	1.0	100.00	0.0	0.00
1.95	0.487	0.513	0.9	91.40	0.1	8.60
1.90	0.474	0.526	0.8	82.53	0.2	17.47
1.85	0.459	0.541	0.7	73.37	0.3	26.63
1.80	0.444	0.556	0.6	63.92	0.4	36.08
1.75	0.429	0.571	0.5	54.15	0.5	45.85

Cement preparation

The six TTCP products with different Ca/P ratio (TTCP/α-TCP mixtures) were mixed with DCPD in equimolar amounts (68.03% (mass percent) of TTCP and 31.97% (mass percent) of DCPD) in a micromill (Bel-Alert Products, Pequannock, NJ) to form six different calcium phosphate cements. Mixtures were referred to as CPC_{2.00} through CPC_{1.75} according to Ca/P ratio of the TTCP component. Two liquid phases were used as the cement liquid. In one set of experiments, distilled water was used as the cement liquid and in a second set of experiments a 0.25 mol/L sodium phosphate solution was used. This sodium phosphate solution was prepared by diluting a 3 mol/L phosphate solution (Na₂HPO₄ and NaH₂PO₄, Abbott Laboratories, North Chicago, IL) with distilled water.

Setting time measurements

Setting time measurements were performed with a 2 × 6 full factorial design in which the two cement liquids were tested with the six cement mixtures prepared. Each powder and liquid was manually mixed with a spatula at a powder to liquid (P/L) ratio of 4.0. The paste was then transferred to a stainless steel mold of 6 mm diameter and 3 mm depth. Each specimen was incubated in a humidior at 37°C and 100% relative humidity for different time intervals and the setting times were checked using a Gillmore needle following the procedure described previously,²⁰ and with ASTM C266-99 as guidance.²¹

pH measurements of the cement mixtures

Measurement of the pH changes in slurries of the different TTCP products as well as the cement mixtures were conducted using the following procedure. About 0.5 g of powder was placed in a test tube and 2 mL of distilled water were added. A small stirring bar was also introduced in the test tube, which was then capped and vortex-stirred for 5 s. The cap was then removed and a pH electrode (Orion Model 91-03 Combination pH Electrode) was inserted into the tube while the slurry was continuously being stirred at 47.12 rad/s (450 rpm). pH changes were directly recorded by means of LabVIEW 5.1 software (National Instruments, Austin, TX) for 3 min, and a replicate

measurement of each sample was performed. The pH electrode was calibrated with pH 7 and pH 11 standards (Fisher Scientific, Fair Lawn, NJ) prior to the experiment and was re-checked with the pH 11 buffer between cement samples.

Preparation of CPC samples for mechanical testing

Cement specimens for mechanical testing were prepared by mixing 0.6 g of cement mixture with 0.15 mL of liquid and the resulting paste was placed in a stainless steel mold (6 mm in diameter, ~12 mm depth, ISO 9917-1 was used as guidance), which was then placed in a constant-pressure loading device described previously.²² In this study a pressure of 5 MPa was applied during 30 s and then the samples were allowed to set for 30 min in the molds. The samples were then removed from the molds and placed in distilled water for another 23.5 h at 37°C before measurements.

Mechanical testing

Compressive strength (CS) was the property selected for evaluating the mechanical performance of the cement mixtures. A 6 × 2 full factorial design was followed in which the six cement mixtures were tested with two cement liquids. Measurements were carried out on wet specimens using a computer controlled Universal Testing Machine (Instron, United Calibration Corp., Garden Grove, CA) at a loading rate of 1 mm/min.

Microstructure evaluation

Scanning electron microscopy (SEM) was used to evaluate the influence of the Ca/P ratio on the morphology of the cements. Initial powder mixtures and fractured surfaces of the set cements were gold coated prior to SEM examination (JEOL, JSM-5300, JEOL USA Inc. Peabody, MA).

Statistical analysis

One standard deviation (SD) is reported in this paper for comparative purposes as the estimated standard uncertainty of the measurements. One-way analysis of variance (ANOVA) was performed on the resulting median particle size with Ca/P ratio being the independent variable. Also,

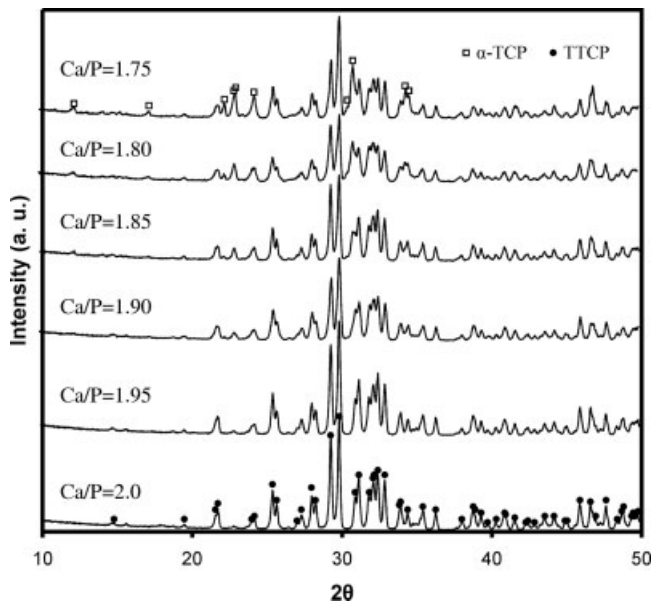


Figure 1. XRD patterns of synthesized TTCP products with different calcium to phosphate ratio. Note that the amount of α -TCP present increased as the Ca/P ratio decreased.

two-way ANOVA was performed on CS with Ca/P ratio and type of cement liquid being the independent variables. Newman-Keuls multiple comparison tests were conducted if a significant difference ($p < 0.05$) existed.

RESULTS

Synthesis of TTCP

XRD patterns of the different TTCP products synthesized are included in Figure 1. It can be seen that as the Ca/P ratio decreased from 2.0, the amount of α -TCP present increased. The peak at $22.89^\circ 2\theta$ corresponding to α -TCP is easily identifiable in the products with higher Ca/P, because it is free from overlapping, and in the lower ratio products the peak at $31.71^\circ 2\theta$, which is in fact the highest intensity peak, was also clearly seen, even though it was partially overlapping a TTCP peak. Table II contains the median particle sizes of the different TTCP products. One way analysis of variance indicated that the Ca/P ratio of the TTCP products had a significant effect on the resulting median particle size. ANOVA found three statistically different groups namely, TTCP_{1.75-1.85}, TTCP_{1.90}, and TTCP_{1.95-2.00}, and the median particle size increased as the Ca/P ratio decreased.

Figure 2 includes the pH measurements performed on the TTCP products with different Ca/P. The pH of TTCP_{2.00} stabilized at a value of 12.25 and TTCP_{1.75} pH stabilized at a value of 9.42, with the rest of the TTCP products falling in between.

TABLE II
Ca/P Ratios and Median Particle Sizes of Synthesized TTCP Products

TTCP	Ca/P	Median Particle Size, Φ (μm)
TTCP _{2.00}	2.00	$16.94 \pm 0.43^{a,b}$
TTCP _{1.95}	1.95	16.37 ± 0.16
TTCP _{1.90}	1.90	18.36 ± 0.01
TTCP _{1.85}	1.85	19.59 ± 0.21
TTCP _{1.80}	1.80	19.36 ± 0.33
TTCP _{1.75}	1.75	19.25 ± 0.28

^aMean \pm standard deviation, $n = 2$.

^bGroups connected with a line are not statistically different, $p < 0.001$.

Figure 3 includes SEM micrographs of the six TTCP-DCPD cement mixtures prepared. TTCP particles with round edges appeared partially covered with smaller, globular DCPD particles. Sintering necks could also be seen. Even though the amount of α -TCP present increased as the Ca/P ratio decreased, as shown with XRD analyses, no significant differences on the morphology of the mixtures could be found that would give any indication as to how these two phases, TTCP and α -TCP, were distributed.

Setting times of the cement mixtures

Table III includes the setting times determined for each of the mixtures with both distilled water and a 0.25M sodium phosphate solution. P/L ratio was 4.0 in all cases. When water was used as the setting liquid, all mixtures had setting times in the range 18–22 min, regardless of the Ca/P ratio and regression analysis showed no linear relation between the Ca/P ratio and the setting time ($r^2 = 0.44$, $p =$

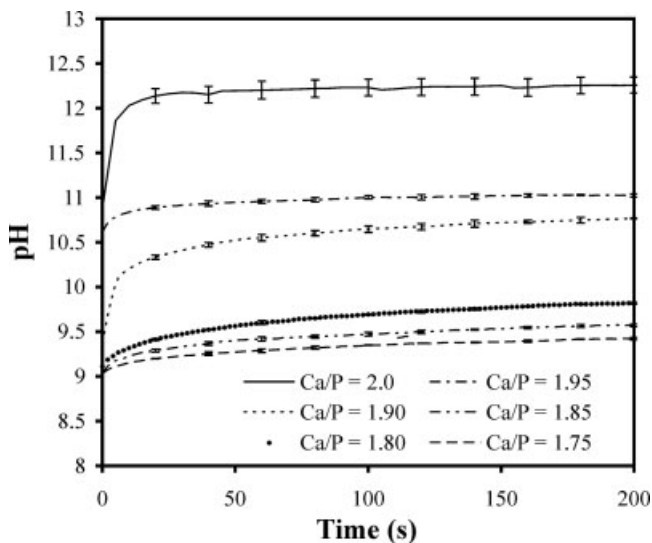


Figure 2. pH measurements of slurries prepared with the TTCP products with different Ca/P ratios. Representative SD bars were included.

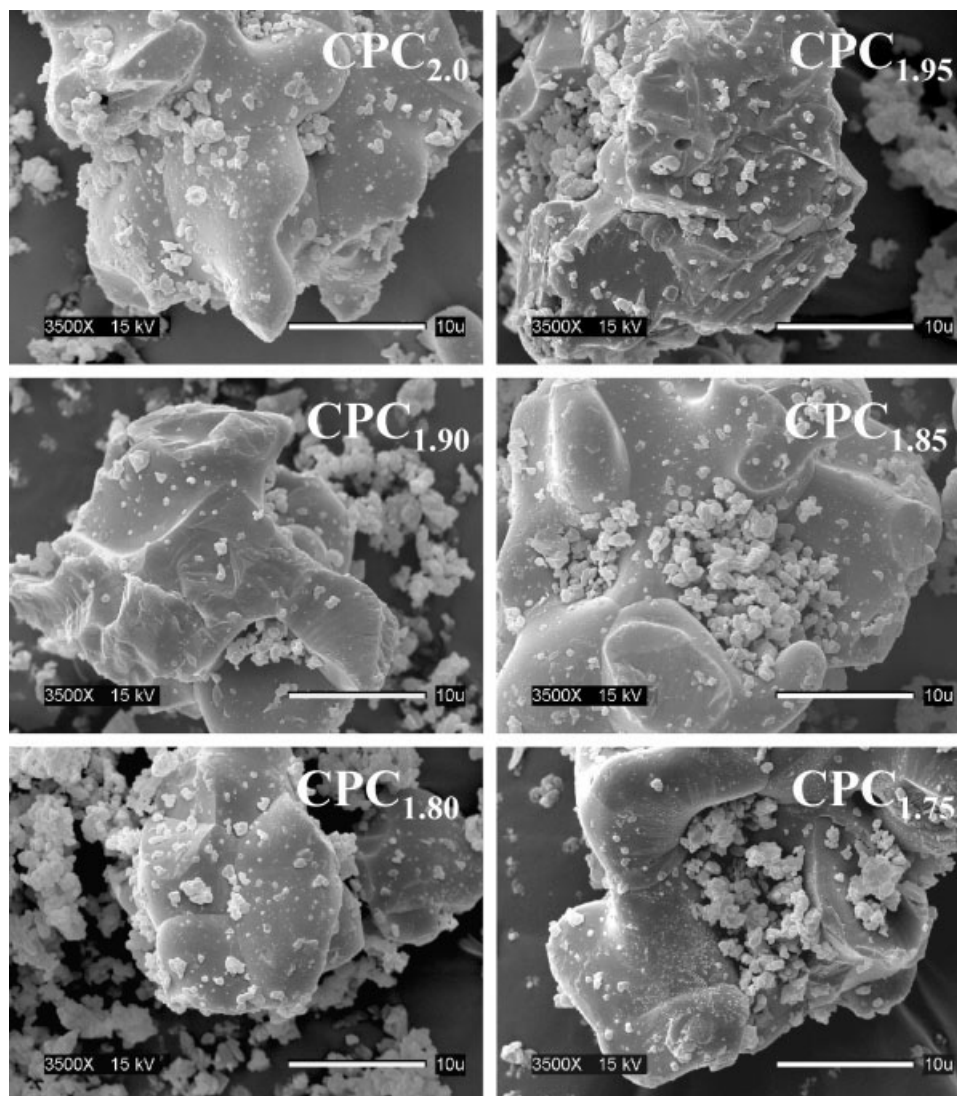


Figure 3. SEM micrographs of CPC powders prepared with DCPD (small globular lighter particles) and TTCP products with different Ca/P ratios (larger, darker particles with rounder edges).

0.152). When phosphate solution was used, all mixtures set in 7–8 min, therefore, Ca/P did not have a marked effect on the setting time when dilute sodium phosphate solution was used.

pH measurements

pH measurements of the six cement mixtures are included in Figure 4. All the pH values were in the 7.2–7.6 range. The same trend as observed with the TTCP products was seen for the mixtures: the pH plateau value decreased as the Ca/P ratio decreased.

Mechanical testing

Table IV contains the CS values obtained for the different TTCP-DCPD cements mixtures. Two-way

TABLE III
Setting Times (ST) of Cements Prepared With TTCP
With Different Ca/P Ratios

Mixture	TTCP/ DCPD	TTCP P/L	ST, water (min)	ST, phosphate (min)
CPC _{2.00}	1:1	TTCP _{2.00}	4.0	18 ^a
CPC _{1.95}	1:1	TTCP _{1.95}	4.0	19.5
CPC _{1.90}	1:1	TTCP _{1.90}	4.0	18.5
CPC _{1.85}	1:1	TTCP _{1.85}	4.0	21.5
CPC _{1.8}	1:1	TTCP _{1.80}	4.0	20.5
CPC _{1.75}	1:1	TTCP _{1.75}	4.0	20

^a*n* = 2, Standard Deviation was <1 min for all values.

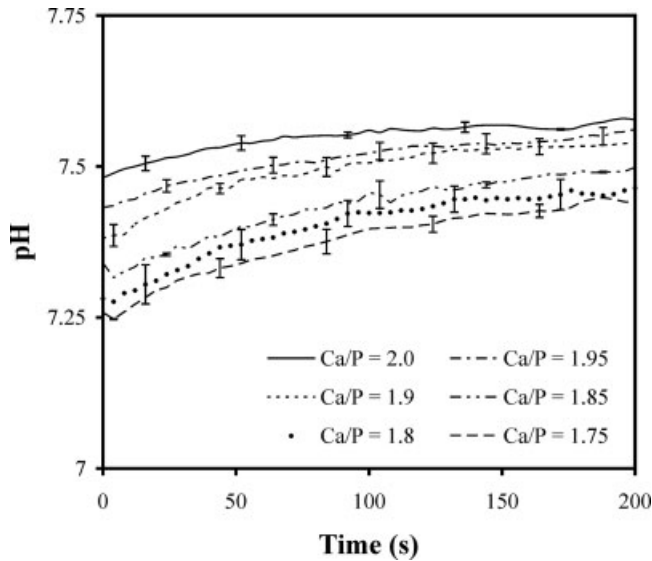


Figure 4. pH measurements of slurries prepared with the different CPC mixtures. Representative SD bars were included.

analysis of variance was performed on mixtures CPC_{1.95} through CPC_{1.75}. Mixture CPC_{2.00} showed a very low CS standing apart from the rest of the values when water was used as the setting liquid. During the preparation of CS specimens it was noted that when CPC_{2.00} was mixed with distilled water at the same powder to liquid ratio as that used for the other mixtures, the resulting paste was very dry and difficult to manipulate to introduce into the molds. This was not the case with the rest of the mixtures or when phosphate solution was used as the setting liquid. This observation, together with the low CS values obtained, suggest that a different mechanism is involved for this mixture (see discussion), and for this reason it was not included in the ANOVA analysis. Both the Ca/P ratio in the TTCP and the type of setting liquid used had a significant influence on the CS of the resulting cements ($p < 0.001$). There were no significant interactions between the two main effects, and multiple comparisons of the marginal means (Table V) showed that CS

TABLE IV
Compressive Strength of Cements Prepared With TTCP With Different Ca/P Ratios

Mixture	CS (MPa)	
	Water	Phosphate
CPC _{2.00} ^a	25.61 ± 2.33 ^b	43.10 ± 3.94
CPC _{1.95}	45.62 ± 3.22	42.11 ± 5.41
CPC _{1.90}	46.70 ± 2.02	39.74 ± 1.90
CPC _{1.85}	38.32 ± 2.37	33.10 ± 1.47
CPC _{1.80}	39.40 ± 2.25	31.81 ± 3.32
CPC _{1.75}	41.83 ± 1.78	32.74 ± 2.67

^aThis mixture was not included in the ANOVA analysis.

^bMean ± standard deviation, $n = 6$.

TABLE V
Multiple Comparisons of Marginal Means of Compressive Strength Data in Table 4

Test Statistic	CS (MPa)
Ca/P ratio ($n = 12$)	
1.95	43.87 ^a
1.90	43.22
1.85	35.71
1.80	35.61
1.75	37.29
Setting Liquid ($n = 30$)	
Water	42.38
Phosphate	35.90

^aGroups connected with a line are not statistically different, $p < 0.05$.

values of cement specimens prepared with water are 15.3% higher than the values of specimens prepared with a sodium phosphate solution as the setting liquid. Also, CS values of CPC_{1.90} and CPC_{1.95} are significantly higher than those of the three lower Ca/P ratios. Although it was not included in the statistical analysis, when the phosphate solution was used as the setting liquid, CPC_{2.00} exhibited a numerically higher CS than those of CPC_{1.95} and CPC_{1.90}.

Conversion to HA

Figure 5 shows the XRD patterns of 24 h set cement specimens of the six TTCP-DCPD mixtures (distilled water as the setting liquid). Mixtures with higher Ca/P ratio had higher conversion to HA.

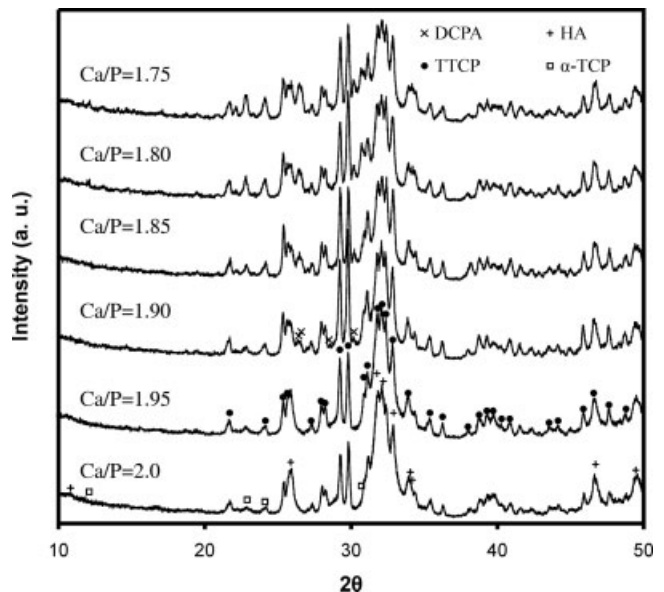


Figure 5. XRD patterns of 24 h set CPC specimens prepared with the TTCP products with different Ca/P ratios and DCPD, and water as the setting liquid. Note that unreacted DCPD converted to DCPA during the drying process prior to the XRD analysis.

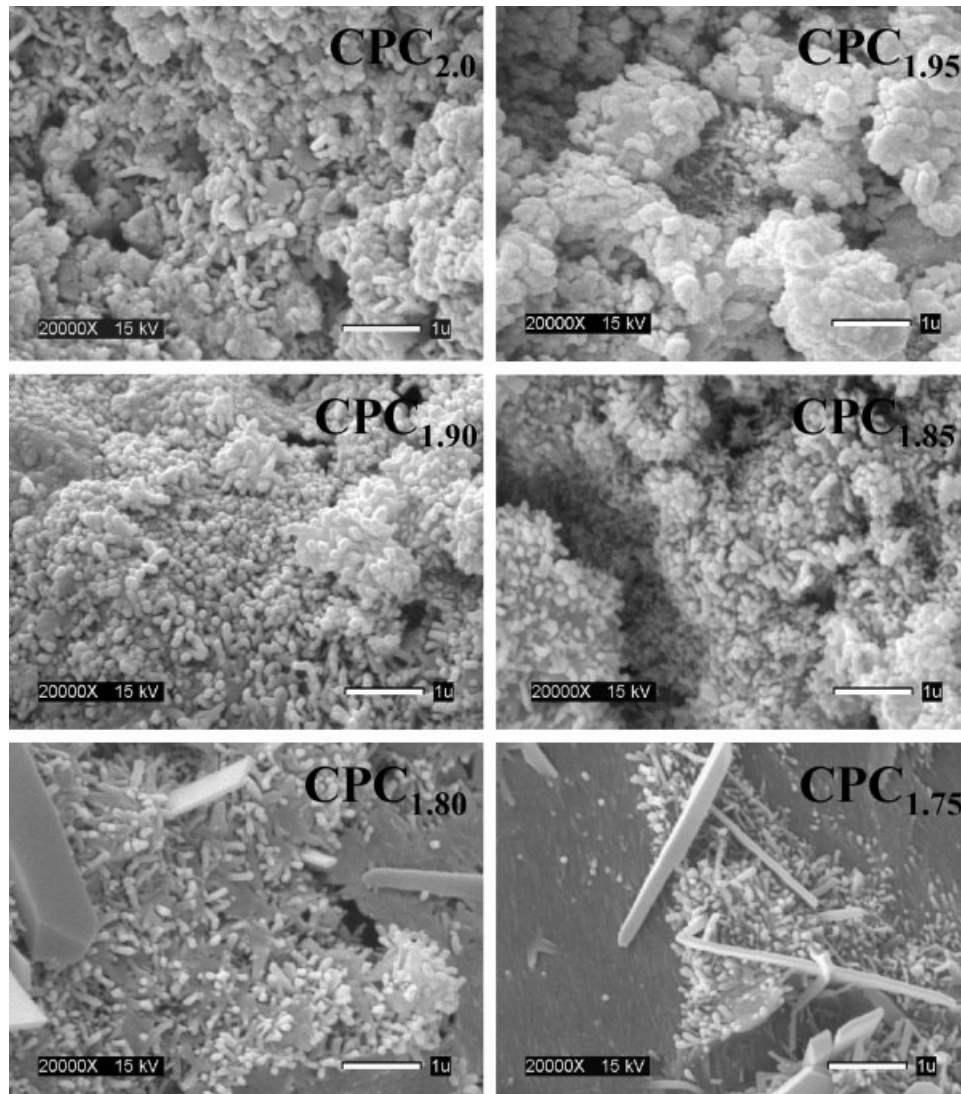


Figure 6. SEM micrograph of fracture surfaces of 24 h set cement specimens prepared with DCPD and TTCP products with different Ca/P ratios, and water as the setting liquid. Small rod like HA crystals were seen in all specimens. Large plate-like crystals which were identified as DCPA crystals were seen in the specimens with lower Ca/P ratios 1.80 and 1.75.

CPC_{2.00} had the highest conversion to HA among the different mixtures. There is a small amount of TTCP left in all the set cements which suggests that the reaction did not reach completion. Unreacted α -TCP could also be seen in the cements with lower Ca/P ratios. Some DCPA was also present in the low Ca/P ratio cements; this phase formed upon drying of the set cements for the XRD analysis, from unreacted DCPD.¹¹ XRD patterns of the 24 h set cements with phosphate as the setting liquid showed lower conversion to HA with evidence of both unreacted TTCP and DCPD (patterns not shown).

Microstructure of the set cement

Figure 6 included SEM micrographs of fracture surfaces of 24 h water set cements. All included

small rod-like crystals which have previously been identified as HA.¹¹ No significant differences could be seen in the morphology of the formed HA among the six different set cements. In the case of CPC_{1.80} and CPC_{1.75} plate-like crystals could also be seen. These plates have been identified as DCPA formed during the drying process prior to SEM examination.¹¹

DISCUSSION

Calcium phosphate cements are promising materials for bone replacement. Many systems have been formulated including combinations of most known calcium orthophosphates in different proportions.⁴ It seems more likely that advances in the performance and broadening of the applications of calcium phos-

phate cements come from improvements or refinements in the components of already known systems rather than from the development of new formulations. In this sense, this study aims to optimize the TTCP component of a TTCP-DCPD cement previously developed.¹¹

Modifying the Ca/P ratio of the starting reagents mixture in the synthesis of TTCP yields different products with varying TTCP/ α -TCP ratio. A Ca/P ratio of 1.90 was used in previous studies to avoid the presence of CaO in the resulting TTCP product,¹⁴ which is known to negatively affect the resulting cement.¹⁶ In the present work two products were synthesized with a higher Ca/P ratio, namely, 1.95 and 2.0 and care was taken to measure and thoroughly homogenize the starting materials to prevent formation of CaO in these two syntheses. In spite of this, and even though it was not observable in the XRD pattern of TTCP_{2.00}, the pH measurements performed suggests that some CaO might have formed. Calculated pH values for solutions saturated with CaO, TTCP and α -TCP were 12.5, 10, and 9.8 respectively (calculated with Chemist, MicroMath Research, Saint Louis, MI, pKsp values used were 5.19, 38, and 25.5 for Ca(OH)₂, TTCP and α -TCP, respectively); therefore, the high pH value obtained for TTCP_{2.00} may be explained by the presence of CaO because, being more soluble than TTCP, it would dominate the pH of the slurry even in a small amount. Slurries prepared with TTCP_{1.95} and TTCP_{1.90} reach values that are consistent with the pH of a solution saturated with TTCP.

On the other hand, pH measurements of the different CPC mixtures yielded very similar values. The presence of both TTCP and DCPD, and the dissolution and reprecipitation reactions taking place maintained the pH close to the singular point value, even when mixtures with TTCP with higher Ca/P tended to produce higher pH values. Several pH values have been reported for the singular point of the TTCP-DCPD system ranging from 7.50 to 8.50,^{4,9} mostly due to the fact that TTCP is very reactive in water and several different solubility products have been proposed in the literature ranging from 10⁻³⁸ to 10⁻⁴⁴.^{9,23} As a result the position of the TTCP isotherm in the phase diagram can vary slightly depending on the Kps value used for its calculation, resulting also in variations of the location of the singular point. The values obtained in the present study (7.25–7.60) are in agreement with the values reported previously.

With respect to the properties of the TTCP-DCPD mixtures prepared, the setting times obtained in the present study, when distilled water was used as the setting liquid, were slightly longer than other values reported for the TTCP-DCPD system in previous studies²⁴; differences in particle sizes observed may

partially contribute to the small differences in setting times when water was used as the setting liquid, both among the mixtures in this study and with respect to previous studies. Setting times obtained when sodium phosphate was used as the setting liquid are in agreement with values reported previously.¹¹ The Ca/P did not have a marked effect on the setting time whether distilled water or dilute sodium phosphate solution were used.

As mentioned, during the preparation of CS specimens it was noted that when CPC_{2.00} was mixed with distilled water at the same powder to liquid ratio as used for the other mixtures, the resulting paste was very dry, and difficult to manipulate and to introduce into the molds, which resulted in very low CS values. This might be another consequence of the presence of CaO. It would be reasonable to assume that its presence would cause an increase in the pH of the setting cement liquid, making it too basic for the reaction to proceed normally. However, the pH experiments performed on the cement mixtures proved that this was not the case. On the other hand CPC_{2.00} showed the highest conversion to HA (when water was used as the setting liquid) among the different Ca/P mixtures. Therefore, if CaO presence hindered the strength development, it was not done by preventing the setting reaction from proceeding [because HA was formed, which was also confirmed by SEM examination (Fig. 6)]. These observations seem to suggest that the presence of CaO somehow affects the cohesiveness of the mixture resulting in a cement with low strength.

Taking this into account, when CPC_{2.00} was again not considered due to the different mechanism involved, and comparing the CS values of mixtures CPC_{1.95} through CPC_{1.75} and their respective set XRD patterns, there seems to be a correlation between conversion to HA and mechanical strength. This would explain why samples prepared with phosphate solution were generally weaker than those prepared with distilled water.

Another important observation derived from the XRD patterns of the set cements is also related to conversion but more specifically to the relative consumption of the reacting components, TTCP and DCPD. No trace of DCPD or DCPA (DCPA formed from unreacted DCPD upon drying) could be seen in the 24 h patterns of CPC_{2.00} and CPC_{1.95}, therefore all DCPD was consumed during the reaction. However, there was a residue of TTCP present in both cases. This indicates that the HA formed is calcium deficient.

As the Ca/P ratio decreased so did the consumption of DCPD. Mixtures with Ca/P of 1.90 and lower have peaks of residual TTCP but also DCPA peaks, which derive from residual DCPD, the intensity of the latter increased as the Ca/P ratio decreases. This

would suggest that the proportion at which TTCP and DCPD were consumed during the setting reaction was not the same in all the mixtures and therefore the apatite products precipitated might have different Ca/P ratios, although the available information is not sufficient to quantify it. It might be expected that the Ca/P ratio of the HA formed was dependent on the local solution composition at the site where the crystals were formed, and this may be affected by several factors such as local calcium and phosphate concentration or local pH.

Also noteworthy is that α -TCP did not seem to take part in the setting reaction as an active reactant; this compound was not consumed appreciably during the setting reaction and therefore, α -TCP peaks remain constant in the set cement. This observation was also made by Xie and Monroe¹⁷ who indicated that α -TCP is not a good cement component because it hardly hydrolyzes in a system composed of a mixture of phases. Because it did not take part in the setting reaction, α -TCP could have acted as a reinforcing phase, but in light of the CS results this was not the case either. However, another possibility is that α -TCP was distributed partially covering the surface of the TTCP particles, making some parts unavailable for reaction. This would also explain why the degree of conversion decreased as its proportion increased in the cement.

SUMMARY

The effects of the overall Ca/P ratio of the TTCP synthesis mixture on the properties of the resulting TTCP-DCPD cement were systematically studied.

It was found that possible CaO formation in the TTCP with a Ca/P ratio of 2.0 resulted in low strength when distilled water was used as the setting liquid even though no direct evidence was found. Lower Ca/P ratios showed CSs in the range 38–46 MPa. XRD analyses showed conversion to HA in all cases with both TTCP and α -TCP leftover.

In terms of cement strength and HA conversion, the best TTCP preparation for formulating a TTCP-DCPD cement appears to be one with the Ca/P ratio closest to 2.0 provided that CaO formation is avoided altogether. TTCP with Ca/P ratios between 1.9 and 1.95 were found to be safe approximations, since they also yielded good setting and mechanical properties and it is ensured that CaO is not present.

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