JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **10** (1999) 223–230

Production and characterization of new calcium phosphate bone cements in the $CaHPO_4$–α-$Ca_3(PO_4)_2$ system: pH, workability and setting times

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The initial setting properties of calcium phosphate cements in the $CaHPO_4$–α-$Ca_3(PO_4)_2$ (DCP–α-TCP) system have been investigated. Interest was focused on the pH, workability, cohesion time and initial and final setting times. The addition of $CaCO_3$ modified the structure of the cement reaction product such that it became more similar to the apatite phase in bone mineral. The addition of 10% w/w of $CaCO_3$ reduced the viscosity of the cement pastes resulting in an increase in initial and final setting times and improved injectability.
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1. Introduction

Calcium phosphates have attracted great attention in medicine and dentistry due to their excellent biocompatibility and bone-repair properties. In fact, the mineral fraction of hard tissues is composed of sparingly soluble calcium phosphates. However, these materials have some disadvantages in clinical applications, such as poor adaptation to the shape of bone cavities and fixation problems when granules are used. These disadvantages may be overcome by the introduction of cement formulations consisting of calcium phosphates. A calcium phosphate cement (CPC) shows the ability to conform perfectly to the defects in hard tissues (tooth, bone, etc.), resulting in the possibility for close apposition to the host tissue. This is as a result of their self-hardening properties which occur through a setting reaction at room or body temperature leading to the formation of a solid precipitated calcium phosphate.

A cement material consists of a solid powder phase which initially forms a plastic paste upon mixing with a liquid phase. This viscous paste will transform to a stiff paste during setting, increasing its mechanical strength progressively up to saturation (hardening). The properties of a cement material such as the initial plasticity, the setting and hardening time, and the final strength can be controlled by factors affecting the powder phase, the liquid phase, the mixture of the powder and the liquid and the aging conditions.

In this study, the initial setting properties of CPCs in the dicalcium phosphate–α-tricalcium phosphate (DCP–α-TCP) system have been investigated. Interest has been focused on the pH, the workability, the cohesion time (CT) and the initial (*I*) and final (*F*) setting times. According to previous results [1], which showed that setting properties in the DCP–α-TCP system are related to an α-TCP hydration process, the effect of the addition of $CaCO_3$ (CC) has been studied since carbonate ions modify the calcium deficient apatite structure of the reaction product to form a phase more similar to the apatite in bone mineral [2].

2. Materials and methods

2.1. Reactants

Commercial-purity grade (CP) DCP (Merck-Ref. 2144) and α-TCP were used as the main reactants. α-TCP was synthesized at high temperature by a 1 : 2 molar mixture of DCP and CC (Merck-Ref. 2076) [1]. CP-grade precipitated hydroxyapatite (PHA; Merck-Ref. 2143) and CC were used in the powder phase as seed material and as a modifying additive, respectively. The phase purity of the reactants was confirmed by X-ray diffraction (XRD; Siemens-D500).

2.2. Particle size and specific surface area

α-TCP was milled to three different particle sizes (A, B and C) by controlling the milling time in an agate ball mill (Pulverisette 6, by Fritsch GmbH) to study the effect of particle size on the setting and hardening properties of

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the cement. Particle sizes were analyzed by a laser diffraction technique (Microtrac SRA-150) and the specific surface area (*S*) was measured by the Brunauer–Emmett–Teller (BET) method (Quantasorb, by Quantachrome Corp.).

2.3. Experimental procedure

The powder phase of the DCP and α-TCP mixtures was adjusted to a calcium to phosphorus ratio (Ca/P) of $1.26 \leq \text{Ca/P} \leq 1.50$. 10% w/w of PHA was added to each sample and the effect of CC on setting properties was studied for 0 and 10% w/w additions in the total DCP–α-TCP mixture. The effect of the water to powder ratio (*W*/*P*) on setting properties was studied for $0.30\,\text{ml}\,\text{g}^{-1}$ and $0.35\,\text{ml}\,\text{g}^{-1}$. Table I summarizes the samples studied (X) and the experimental conditions under which they were prepared. Accelerators were not used in the liquid phase because they result in a reduction in the mechanical properties [3].

2.4. pH measurements

A computer controlled pH meter (Metrohm-691, by Metrohm Ltd) was used. The study was conducted for the B-series samples (see Table I) with and without CC additive to study the effect that CC has on the pH solution and how this affected the reactivity of the cement powder phases. The *W*/*P* ratio used was $35\,\text{ml}\,\text{g}^{-1}$. Data acquisition continued for a period of 9 h from an initial value of the pH solution of pH = 7.

2.5. Workability, cohesion time and setting times

The criterion for a cement to be workable was as follows. A cement was workable and thus suitable for injection when a homogeneous paste with an acceptable wettability of the powder by the liquid was formed when mixing the powder and the liquid phases. A cement was not workable when, after mixing the powder and the liquid, an inhomogeneous and dried paste was formed with poor powder wettability.

TABLE I Preparation conditions (Ca/P ratio, CC%, milling times, *W*/*P* ratio) investigated for the experimental cements

		W/P = 0.30			W/P = 0.35		
Ca/P	CC(%)	A	B	C	A	B	C
1.26	0	X	X	X	X	X	X
1.28	0	–	X	X	X	X	X
1.30	0	X	–	X	–	X	–
1.32	0	–	X	X	X	X	X
1.34	0	X	–	X	–	X	–
1.36	0	–	X	X	X	X	X
1.38	0	X	–	X	X	X	–
1.40	0	–	X	X	X	X	X
1.42	0	X	X	X	–	X	X
1.50	0	X	X	X	X	X	X
1.26	10	–	X	–	–	X	–
1.30	10	–	X	–	–	X	–
1.34	10	–	X	–	–	X	–
1.38	10	–	X	–	–	X	–
1.42	10	–	X	–	–	X	–
1.50	10	–	X	–	–	X	–

CT was measured according to the visual method with time control developed by Fernandez *et al.* [4]. *I* and *F* were measured with Gillmore needless (ASTM C266-89).

3. Results

3.1. Particle size and specific surface area

Fig. 1 shows the cumulative particle size distributions measured for the α-TCP for the different milling conditions used. The cumulative volume distribution gives the percentage of the total volume (*y*-axis) of the sample formed by particles having lower size than the corresponding value on the abscissa. The median particle size, *d*(0.5), (the particle size for which 50% of the sample volume is formed by particles smaller than the median) and the values *d*(0.1) and *d*(0.9) are summarized in Table II for the α-TCP as well as for the other reactants.

Table II also shows the results of the specific surface area (*S*) for the α-TCP, responsible for the hydration reaction in the DCP–α-TCP system [1]. It can be seen that the *S* of α-TCP increases with milling time (A < B < C), as might be expected. However, milling conditions A and B gave quite similar values of *S* and quite different from milling condition C.

3.2. pH measurements

Fig. 2 summarizes the results of pH variation with time for the powdered reactants in neutral, deionized water.

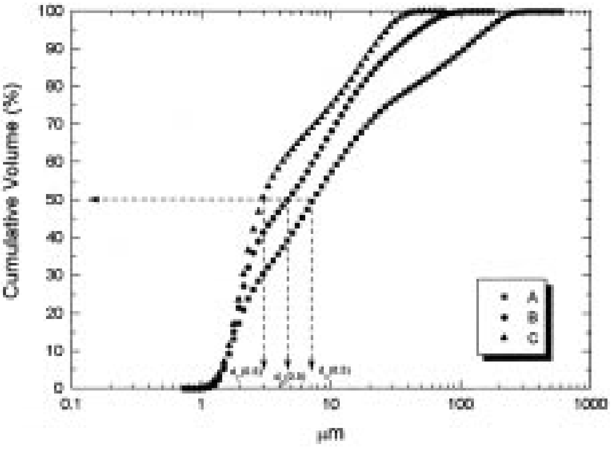

Figure 1 Cumulative particle size distributions (volume %) for α-TCP under different milling conditions (A = 1; B = 2; C = 4 h).

TABLE II Particle size and specific surface area measurements for the different reactants used in the DCP-α-TCP cement system

	d(0.1) (µm)	*d*(0.5) (µm)	*d*(0.9) (µm)	*S* ($\text{m}^2\,\text{g}^{-1}$)
α-TCP (A)	1.7	7.3	106.0	1.49 ± 0.04
α-TCP (B)	1.7	4.6	31.8	1.65 ± 0.04
α-TCP (C)	1.7	3.0	20.4	7.24 ± 0.08
DCP (as received)	2.0	22.1	70.0	–
PHA (as received)	2.1	4.5	14.0	–
CC (as received)	11.1	22.6	42.8	–

The basicity of the cement components in ascending order was established to be PHA < DCP <α-TCP < $CaCO_3$. The initial decrease in pH in the PHA–H_2O system from pH = 7 to pH ≈ 6.25 was due to the partial dissolution of PHA at pH = 7 until equilibrium was reached. The PHA was in a stable equilibrium with the aqueous solution at a value of pH = 6.35. Similar results were found for the DCP–H_2O system. The initial increase in pH was due to the partial dissolution of the DCP at pH = 7 until equilibrium with the aqueous solution was reached. The equilibrium pH value for DCP was pH = 7.5. The α-TCP–H_2O system showed an increase in pH to 9.6 due to the initial dissolution of the α-TCP at pH = 7. Over the time interval studied $(0 < t < 9\,h)$ the pH of the aqueous solution decreased gradually from pH = 9.6 to pH = 8.6. This gradual and quasi-constant decrease was related to a very slow α-TCP hydration process. The $CaCO_3$–H_2O system showed an increase in pH to 9.8 due to the initial dissolution of $CaCO_3$ at pH = 7. After this increase the pH decreased gradually, reaching a value of pH = 8.8 after 9 h. This decrease in pH was related to a gradual decrease in the CO_2 partial pressure in the aqueous solution.

Readings of the pH variation with time were taken for the samples from Table I for Ca/P ratios of 1.26, 1.34, 1.42 and 1.50, all without (0%) and with (10%) CC and in the B milling condition. Samples were coded respectively as B-Ca/P-CC. Ca/P ratios 1.26 and 1.50 represent, respectively, the lower and the upper limits of the pH variation with time for all the Ca/P ratio values studied. Results are summarized in Fig. 3 for samples without CC and in Fig. 4 for samples with CC. As can be seen from Fig. 3, the addition of 10% w/w PHA to α-TCP (sample B-1.50) resulted in a general decrease in the pH of the solution with time as compared with pure α-TCP under the same milling conditions (see Fig. 2). Similarly, an increase in DCP and a decrease in α-TCP in the cement samples (with the total amount of DCP and α-TCP constant) resulted in a decrease in the pH of the solution. However, for a given Ca/P ratio the pH of the solution was partially increased when 10% w/w CC was added to the DCP–α-TCP mixture (see Figs 4 and 5 for a detail on sample B-1.34).

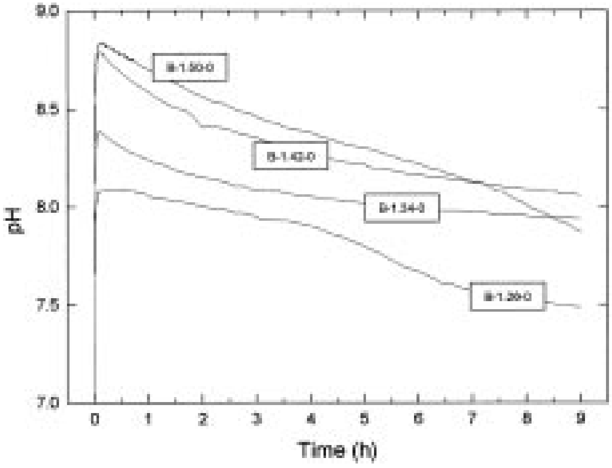

Figure 3 pH variation with time for the cement samples without CC.

3.3. Workability, cohesion and setting times

The results concerning the workability, the CT and the *I* and *F* setting times are summarized in Figs 6–13, as a function of the Ca/P ratio of the cement samples.

Figs 6–8 summarize the results for the *W*/*P* ratio of $0.30\,ml\,g^{-1}$ and for each milling condition of the α-TCP. At this *W*/*P* ratio the cement pastes were not workable, irrespective of their chemical compositions or the milling conditions used for the α-TCP. CT was independent of the Ca/P ratio of the mixture but was dependent on the α-TCP milling conditions. CT measured for milling conditions A and B was 15 min and was 20 min for milling condition C, for virtually all Ca/P ratios tested.

Figs 9–11 summarize the results for the *W*/*P* ratio of $0.35\,ml\,g^{-1}$ and for the different α-TCP milling conditions. Fig. 9 shows the results for milling condition A. During the preparation of this cement sample series a workability limit was observed at a Ca/P ratio of 1.39. Cement pastes were non-workable for Ca/P < 1.39. For Ca/P < 1.39 the CT decreased to 8 min and *I* was higher than CT. These results showed that the *W*/*P* ratio and the Ca/P ratio were correlated.

Fig. 10 shows the results for milling condition B. Under this milling condition the cement pastes were workable for all the Ca/P ratios. The pastes showed the same cohesion properties (CT = 8 min) as for milling

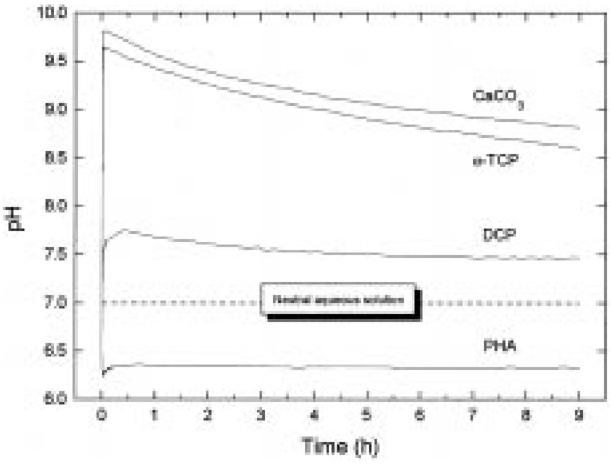

Figure 2 pH variation with time for the main reactants and additives for the DCP–α-TCP cements. ($W/P = 35\,ml\,g^{-1}$).

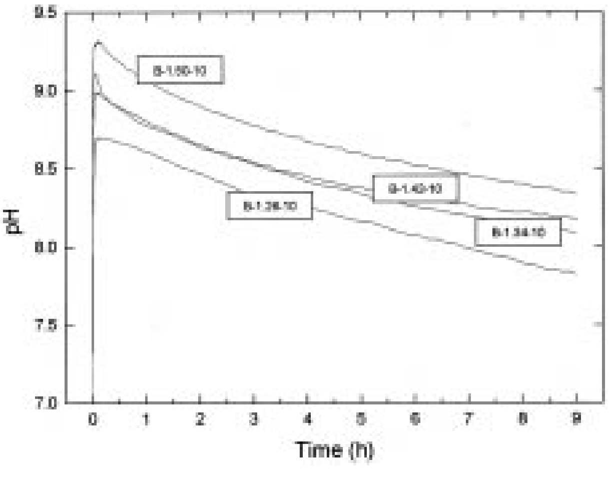

Figure 4 pH variation with time for the cement samples with CC.

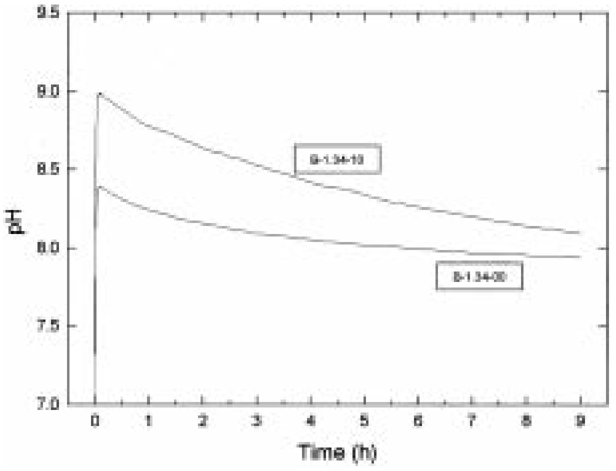

Figure 5 Effect of 10% CC addition on the pH variation with time for the cement sample B-1.34.

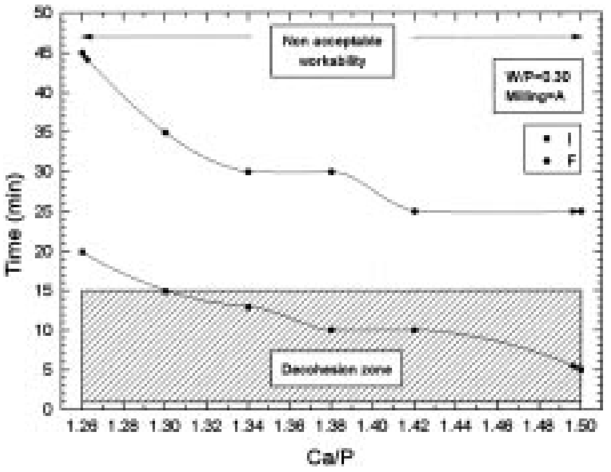

Figure 6 Decohesion zone, workability and setting times versus Ca/P ratio of the cement samples at a *W*/*P* ratio of 0.30 ml g^{-1} under milling condition A.

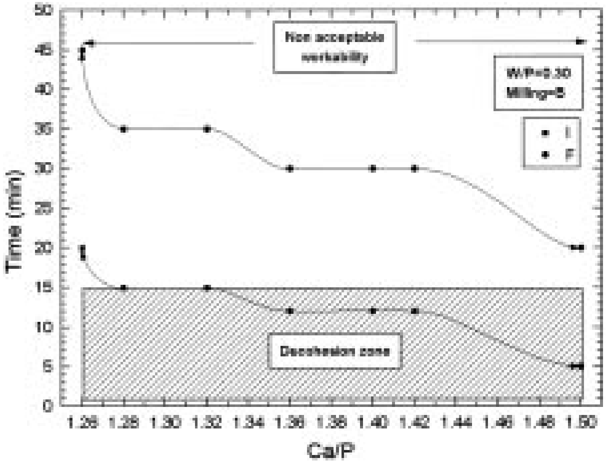

Figure 7 Decohesion zone, workability and setting times versus Ca/P ratio of the cement samples at a *W*/*P* ratio of 0.30 ml g^{-1} under milling condition B.

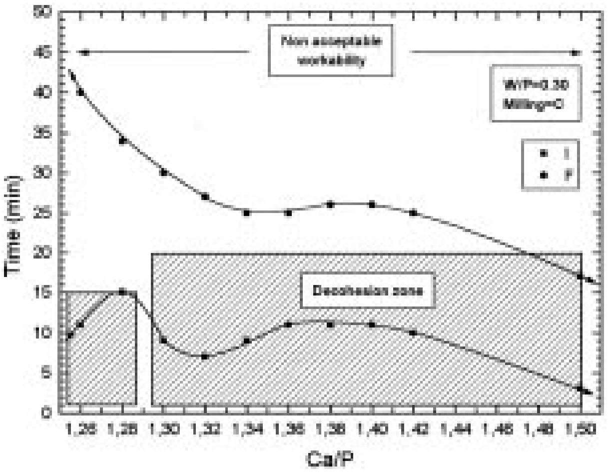

Figure 8 Decohesion zone, workability and setting times versus Ca/P ratio of the cement samples at a *W*/*P* ratio of 0.30 ml g^{-1} under milling condition C.

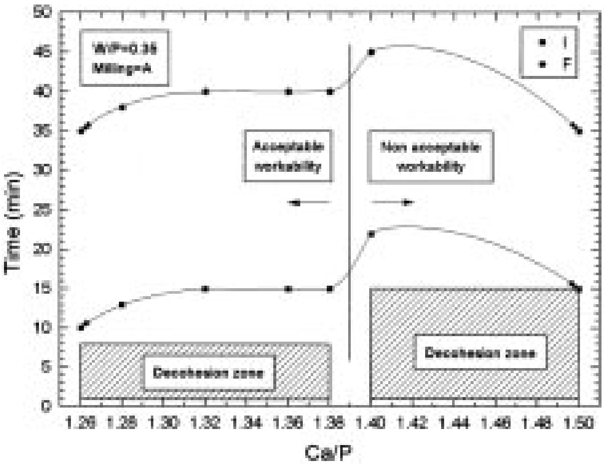

Figure 9 Decohesion zone, workability and setting times versus Ca/P ratio of the cement samples at a *W*/*P* ratio of 0.35 ml g^{-1} under milling condition A.

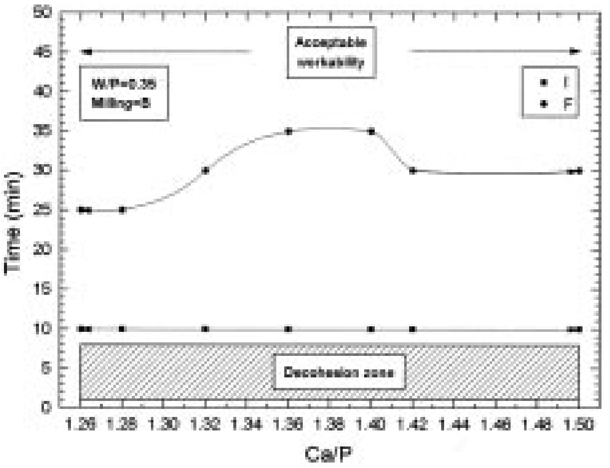

Figure 10 Decohesion zone, workability and setting times versus Ca/P ratio of the cement samples at a *W*/*P* ratio of 0.35 ml g^{-1} under milling condition B.

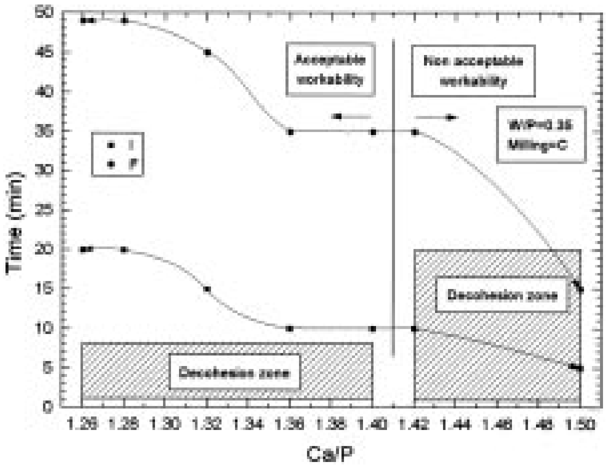

Figure 11 Decohesion zone, workability and setting times versus Ca/P ratio of the cement samples at a *W*/*P* ratio of 0.35 ml g^{-1} under milling condition C.

condition A in the interval Ca/P < 1.39. Also, it was observed that CT < I for all the workable cements. CT and *I* were independent of the Ca/P ratio of the mixture.

Fig. 11 shows the results for milling condition C. A limit at a Ca/P ratio of 1.41 was observed for the workability of the pastes, as mentioned above. For Ca/P > 1.41 the pastes were non-workable and CT increased up to 20 min. For Ca/P < 1.41 the pastes were workable and CT was approximately 8 min. Again, in the workable zone, the relation CT < I applied.

It is interesting to note comparing Fig. 9 with Fig. 10, that the Ca/P ratio and the α-TCP milling condition were related such that a decrease in the α-TCP particle size (from milling condition A to B) moves the limit of workability at all the Ca/P ratio intervals resulting in a decrease in the setting times. Moreover, the relation CT < I also applies. However, comparing Fig. 10 with Fig. 11 it may be observed that increasing the milling time of the α-TCP (changing from milling condition B to C) produced a return of the limit of workability such that in the workable zone (1.26 < Ca/P < 1.41) the effect of the milling condition on the magnitude of the setting times was different for each Ca/P ratio and tended to increase for those mixtures with Ca/P < 1.35.

The effect of the addition of CC on workability, CT and *I* and *F* setting times was investigated at a *W*/*P* ratio of 0.35 ml g^{-1} in the series where α-TCP was milled under condition B. That series was selected because at these experimental conditions cement pastes were initially workable in all the Ca/P ratio intervals (see Fig. 10). As a comparison, samples at a *W*/*P* ratio of 0.30 ml/g and in the B milling condition were also investigated (see Table I). The results are summarized in Figs 12 and 13.

Comparing Fig. 7 with Fig. 12 it can be observed that the addition of 10% of CC moved the limit of workability (in the interval 1.26 < Ca/P < 1.50) to the right to higher Ca/P ratio values up to a value of 1.32. However, CT was not improved in the new workable zone. Comparing Fig. 10 with Fig. 13 it is observed that CT was not affected by the addition of CC. However, in that case, the setting times increased and were independent of the Ca/P ratio. The addition of CC increased the fluidity of the pastes and acted as a reaction retarder. It is expected that this effect would also influence the mechanical properties. However, as far as the setting times are concerned it is possible to control the values of the setting times within acceptable limits for clinical applications with a solution with 4% w/w of Na_2HPO_4 added as an accelerator. The results are summarized in Fig. 14. Working with this solution CT and *I* and *F* setting times were halved as compared with the results obtained in Fig. 13 and were independent of the chemical composition of the mixtures.

4. Discussion

The specific surface area of a powder is an important parameter in the development of cement type materials. According to the Wenzel law [5] the reaction velocity between solids and liquids is proportional to their contact surface. Therefore, it may be deduced that for milling condition C, faster setting cements will result. However, it is known that capillary forces are inversely proportional to the capillary diameter and that this is directly proportional to the particle size [6]. As a consequence,

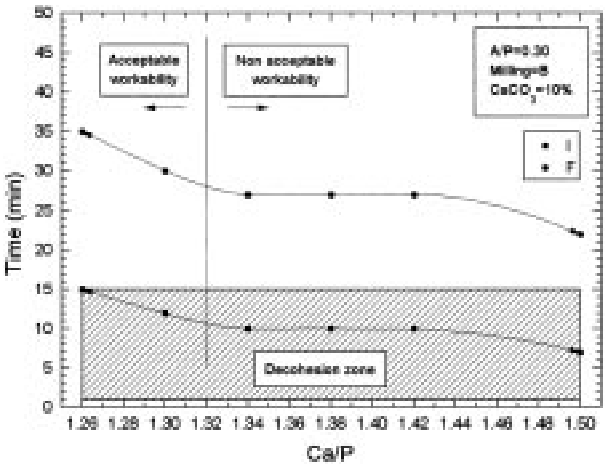

Figure 12 Decohesion zone, workability and setting times versus Ca/P ratio of the cement samples with 10% of $CaCO_3$ at a *W*/*P* ratio of 0.30 ml g^{-1} under milling condition B.

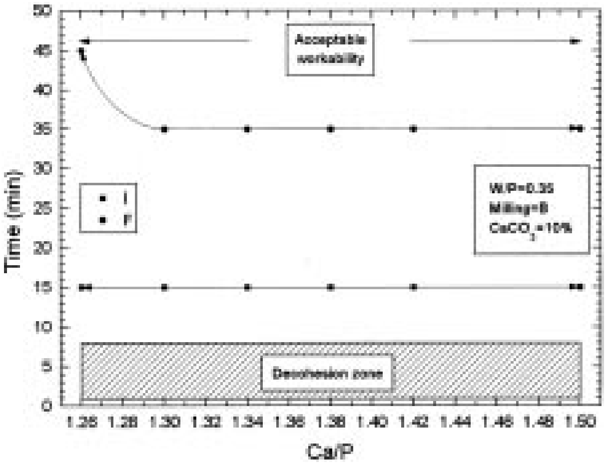

Figure 13 Decohesion zone, workability and setting times versus Ca/P ratio of the cement samples with 10% of $CaCO_3$ at a *W*/*P* ratio of 0.35 ml g^{-1} under milling condition B.

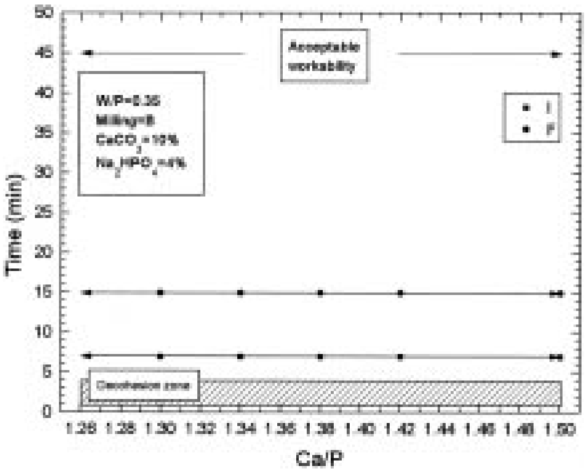

Figure 14 Effect of the addition of 4% w/w Na_2HPO_4 in the liquid phase on the decohesion zone, the workability and the setting times of the cement samples with 10% of CC at a W/P ratio of 0.35 ml g^{-1} under milling condition B.

the CT of cements prepared with the C milling condition for the α-TCP might be expected to be higher.

A study of pH variation with time gives data about the kinetics of the dissolution and precipitation processes of the reactants and products of the cement mixture and this would normally be performed at a W/P ratio higher than the W/P ratio used in the cement. However, the conclusions obtained from this procedure can be extrapolated to the real situation of the cement paste [7–12].

The cement pH is the main factor controlling calcium and phosphorus concentrations in the cement solution. The solution pH affects the rates of the cement setting reactions. Parameters affecting the pH variation during cement setting include: the chemical composition of the main constituents of the cement [3–10, 13–18], the relative proportion of the reactants in the mixture [9, 11], the relative particle size of the main cement components [16], the seed material used and its relative proportion [7, 8, 17], the particle size of the seed material [7, 8], the use of accelerators or retarders in the liquid phase and their relative concentration [3, 7, 8, 10, 15, 19], the liquid-to-powder ratio [7, 8] and temperature [10, 19, 20]. By studying the pH variation with time, additional data may be obtained concerning which phases control setting and at which time. These data can be analyzed with thermodynamic solubility diagrams [21, 22] and can be confirmed with kinetic studies of the setting reaction, using X-ray diffraction (XRD) or calorimetric techniques [1, 23–27].

Important conclusions can be obtained from the results shown in Fig. 2. According to the solubility isotherms of calcium phosphates and their expected thermodynamic behavior [21, 22] it may be deduced that increasing additions of α-TCP in the DCP–H_2O system will increase the solution pH and hence the dissolution–precipitation process of DCP will be accelerated. Conversely, increasing additions of DCP in the α-TCP–H_2O system will decrease the solution pH and hence the dissolution–precipitation process of α-TCP will be accelerated [21, 22]. Thus, from a thermodynamic point of view, it might be expected that this complementary effect could result in certain mixtures of DCP and α-TCP where both effects will be maximum.

Therefore, it can be deduced that the addition of CC would be advantageous for the DCP–H_2O system but it would be a disadvantage for the α-TCP–H_2O system, as was indicated in the analysis of the hardening curves [2]. Similarly, in the DCP-H_2O system the addition of PHA suppressed DCP supersaturation with respect to hydroxyapatite (HA) resulting in a deceleration of the dissolution–precipitation processes. However, for the α-TCP–H_2O system, the addition of PHA increased the supersaturation of α-TCP with respect to the HA and the dissolution-precipitation processes was accelerated [21, 22]. This has been proved by studying the effect of the addition of PHA on the setting times in certain cements [13, 14, 28–30].

The combination of all these effects in the same cement presented many difficulties in predicting the thermodynamic behavior of the whole system. Moreover, kinetic factors are involved and these represent the key to understanding the resulting setting and hardening properties of a CPC [1].

Therefore, in complicated systems such as CPCs where many reactants can interact (DCP, α-TCP, PHA, $CaCO_3$), studies of pH variation with time provide information concerning the relative stability of each component in the cement. In simpler CPC systems (with only two components) pH variation with time may be sufficient to predict the kinetics of the system and the order in which each phase was controlling the setting reactions [9, 10, 15, 31]. However, it is impossible to extrapolate the data to predict the future setting and hardening cement behavior with the only consideration of the pH variation with time. In the current system, some thermodynamic conclusions concerning the retardation effect of the hydration process of α-TCP by the addition of CC can be obtained, taking into account the results of a previous study [1] (where, for certain mixtures of DCP and α-TCP the α-TCP was the only reactive phase). The addition of CC into the total mixture of DCP and α-TCP retarded the hydration of α-TCP and therefore the setting and hardening properties of the cement were also retarded. Moreover, it is expected that carbonate ions are incorporated into the apatitic structure [32] of the reaction product which may result in further improvements in the final mechanical properties.

The term ''workability'' describes the ease with which a cement can be placed and compacted. Although this term is clearly defined for cements such as those used in civil engineering applications [33], there are currently no data available in the literature for determination of workability of CPCs, and most investigators use subjective visual criteria. The same problem is true of measurements of ''injectability'' where researchers modify the material to be injectable through a syringe of a certain diameter [34]. There are currently no data available concerning the viscosity of CPCs although these studies are important to correlate the rheological properties with the initial setting properties of the cement, also known as the plastic–stiff paste transition [35] which is characterized by CT, and I and F setting times.

CT has been defined [4] as the minimum time after which a CPC can be immersed in a saline solution at 37 °C without disintegration. This is the first parameter to consider when a CPC is designed to be used in clinical applications. Recently, Ishikawa *et al.* [36] and Takechi *et al.* [37] developed a cement consisting of a mixture of tetracalcium phosphate (TTCP) and DCP [38]. However, these cements disintegrated when immersed in physiological fluid immediately after cement paste formation. Fernandez *et al.* [4] proposed some techniques for the measurement of CT and found that visual inspection with time appeared to be sufficient to characterize the parameter, which, in clinical practice, would be easy to perform.

I and *F* are also defined in terms of clinical applications. However, although standards are not available specifically for CPCs, procedures for measuring the setting times of conventional and dental cements (ASTM C191-92 and ASTM C266-89) are normally accepted. These standards measure the time period between the initial mixing of the solid and the liquid phases and the point at which the cement paste can withstand a fixed static pressure exerted by a needle without an appreciable indent on the cement surface. ASTM standard C266-89 (Gillmore needles) has the advantage that it gives two time points. In some cases [39] *I* has been related to the time required by the surgeon to mold the cement paste without causing a serious damage to the initial physical cement structure. *F* has been related to the time that the surgeon would have to wait before the wound could be closed whereby some pressure could be exerted without causing serious damage to the cement microstructure.

Practical experience shows that CPCs can readily be prepared in a mortar with a spatula. Clinical experience with dental cements and with polymethylmethacrylate (PMMA) cements shows that the time needed to prepare a homogenous cement paste of the correct consistency should not be more than 1 min. Moreover, *I* should not be less than 4 min, taking into account the period of time ($\approx$ 3 min) after mixing the powder and the liquid phases, that is needed to transfer the cement paste into the patient. The transfer can be made by hand or using a syringe and when using a syringe, an *I* of 8 min is considered sufficient. After transfer, it is desirable that *F* is achieved as soon as possible. Clinical experience reported by some investigators [28] have led to the definition of suitable time intervals for *I* of ($4 < I < 8$ min) and for *F* of ($10 < F < 15$ min), and these limits can be used in the design of new calcium phosphate bone cements (CPBC).

It should be taken into account that setting times will depend on all factors involved in the cement manufacture. First of all, the setting times will depend on the liquid to powder (*L/P*) ratio of the cement mixture [17, 40] and an increase in the *L/P* ratio would be expected to increase the setting times. However for the seed material content [13, 14], the amount of accelerator added to the liquid phase [40, 41] and temperature [42], an increase in these factors would diminish the setting times. Setting times would also be expected to be dependent on the particle size of the reactants, the crystallinity and particle size of the seed materials, the relative proportion of the main reactants in the cement mixture and moisture content. However, as yet no data have been published explaining the effects of these factors and their influence on setting times. What seems clear from practical experience with CPCs is that there is a strong correlation between the setting times and the mechanical properties of the cement. This means that when a cement is designed to minimize the setting times, then the compressive strength is also at a minimum and when the same formulation is designed to obtain maximum compressive strength, then the setting times are increased. A compromise between these properties is therefore necessary to ensure that the CPC is suitable for clinical applications.

5. Conclusions

The study of the initial setting properties of CPBCs in the DCP-α-TCP system showed that:

1. By increasing the *W/P* ratio from 0.30 to $0.35\,\mathrm{ml\,g^{-1}}$ more cement mixtures with higher Ca/P ratio were workable.
2. The value of CT for samples with a workable Ca/P ratio was 8 min and for unworkable samples, the value was 15–20 min.
3. An increase in the *W/P* ratio increased the setting times where the cement paste was workable and where the relation $\mathrm{CT} < I$ applied.
4. A decrease in particle size in the α-TCP cement powder increased the CT of the cement samples at a *W/P* ratio of $0.30\,\mathrm{ml\,g^{-1}}$ However, at a *W/P* ratio of $0.35\,\mathrm{ml\,g^{-1}}$ a decrease in the α-TCP particle size improved the workability of the cement pastes up to a critical value. Where the particle size was below the critical value the workability of the cement pastes was reduced.
5. The addition of CC improved the fluidity of the cement pastes and acted as a setting reaction retarder. An increase in the CC addition can be correlated with an increment in the setting times where the workability of the paste is acceptable and where the relation $\mathrm{CT} < I$ applies.
6. The CT was independent of the addition of CC.

Acknowledgment

This work was supported by a European Grant TMR # ERBFMBICT961621. Further, the authors thank the CICYT (Dirección Científica y Técnica of Spain) for funding this work through project MAT94-0911. The EPSRC are gratefully acknowledged for their support of the IRC in Biomedical Materials.

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Received 24 September 1997
and accepted 3 August 1998