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New hydraulic cements based on α-tricalcium phosphate–calcium sulfate dihydrate mixtures

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Abstract

Calcium sulfate dihydrate (CSD) powder was added to a cement consisting of α-tricalcium phosphate (α-TCP) and water. The changes of the physico-chemical properties of the cement were investigated as a function of the CSD amount, the phosphate concentration in the mixing solution, and the solution volume. An increase of the phosphate concentration in the mixing liquid and small additions of CSD powder strongly reduced the cement setting time. Simultaneously, the fraction of unreacted α-TCP powder present after 1 day of incubation increased, indicating that α-TCP hydrolysis was inhibited. The effects of the CSD amount and the phosphate concentration were synergetic, i.e. the effect of CSD powder was increased with an increase of the phosphate concentration and vice versa. Interestingly, none of the factors affected the cement diametral tensile strength. The present results were explained based on solubility calculations. The present study shows that the use of CSD crystals in combination with phosphate ions is an easy and interesting way to control the setting time of α-TCP–water mixtures, in particular, because the mechanical properties of the cement are not modified.

Keywords: Cement; Calcium phosphate; Calcium sulfate; Physico-chemical properties

1. Introduction

Calcium sulfate hemihydrate ($CaSO_4 \cdot 0.5H_2O$; CSH) and α-tricalcium phosphate (α-TCP; α-$Ca_3(PO_4)_2$) are both a bone substitute and a hydraulic cement. The corresponding setting reactions are:

$$CaSO_4 \cdot 0.5H_2O + 1.5H_2O \rightarrow CaSO_4 \cdot 2H_2O, \quad (1)$$

$$3\alpha\text{-}Ca_3(PO_4)_2 + H_2O \rightarrow Ca_9(PO_4)_5(HPO_4)OH. \quad (2)$$

Despite this analogy, very little has been done to combine these cements. Most efforts have been focused on other systems such as α-TCP–dicalcium phosphate dihydrate (DCPD)–water [1], and α-TCP–dicalcium phosphate (DCP)–water [2,3]. Recently, Nilsson et al. investigated mixtures of α-TCP, CSH, and water [4]. These results showed that α-TCP, CSH, and water could be combined in all proportions to lead to biphasic cements consisting of an entanglement of calcium sulfate dihydrate (CSD; $CaSO_4 \cdot 2H_2O$) and calcium-deficient hydroxyapatite (CDHA; $Ca_9(PO_4)_5(HPO_4)OH$) crystals.

A slightly different approach is to use CSD instead of CSH. First, CSD is chemically and crystallographically very similar to DCPD ($CaHPO_4 \cdot 2H_2O$) [5]. Therefore, CSD could be used to replace DCPD or DCP ($CaHPO_4$) to improve the injectability of CPCs [6]. Second, CSD is a relatively soluble calcium-rich phase. Thus, CSD could be used to accelerate the setting reaction of calcium phosphate cements (CPC) by providing a fast-releasing calcium source. So far, this concept has only been used with a very soluble calcium salt such as $CaCl_2$ [7,8] or with phosphate ions [9]. Third, as CSD is simultaneously a calcium-rich phase and a relatively soluble phase, CSD should eventually dissolve in vivo and react with the phosphate ions present in body fluids to form CDHA or hydroxyapatite (HA; $Ca_{10}(PO_4)_6(OH)_2$) crystals (or a mixture):

$$9CaSO_4 \cdot 2H_2O + 6HPO_4^{2-} \rightarrow Ca_9(PO_4)_5(HPO_4)OH + 6H^+ + 9SO_4^{2-} + 17H_2O, \quad (3)$$

$$10CaSO_4 \cdot 2H_2O + 6HPO_4^{2-} \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 8H^+ + 10SO_4^{2-} + 18H_2O. \quad (4)$$

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These reactions could potentially lead to the replacement of CSD crystals by pores and to the growth of neighboring apatite crystals. Considering these putatively good properties of CSD and the absence of studies devoted to this topic, the goal of this article was to assess the effect of CSD on α-TCP–water mixtures. A particular emphasis was set on the setting time and the evolution of the cement properties over time.

2. Materials and methods

Several series of experiments were performed where the following factors were varied: (i) the CSD fraction; (ii) the concentration of disodium hydrogen phosphate dihydrate (DSHPD; $Na_2HPO_4 \cdot 2H_2O$) in the mixing liquid; and (iii) the amount of mixing liquid. The experiments were performed according to several series of measurements. All experiments were randomized and repeated at least twice.

2.1. Chemicals

α-TCP powder was obtained from Mathys Medical (Bettlach, Switzerland). Its specific surface area was $0.78 \pm 0.03\,m^2/g$ (95% confidence level). This powder was ground for 15 and 60 min (Lab planetary mill, Pulverisette 5, Fritsch, Germany) to obtain two new powders with the specific surface areas of 1.07 ± 0.03 and $1.84 \pm 0.07\,m^2/g$. The powder-to-liquid ratio of the cements made with these powders was 2.32 g/ml. According to the X-ray diffraction (XRD) pattern, the purity of the α-TCP powders was not significantly modified by the grinding procedure and was superior to 98%. Small amounts of HA were detected. The CSD was purchased from Fluka (Art No. 21244, Buchs, Switzerland). Its purity was close to 100% as assessed by XRD. The phosphate buffer solution (PBS) was made using demineralized water and the following salts: 9.0 g/l DSHPD (Fluka, Art No. 71645), 1.79 g/l potassium dihydrogen phosphate (Fluka, Art No. 4873), 4.5 g/l sodium chloride (Merck, Art No. 1.06400), and 0.02 g/l sodium azide (Fluka, Art No. 71290).

2.2. Mixing and preparation

Each cement containing 4.0 g powder (α-TCP + CSD) and 1.72 ml solution was mixed for 45 s with a spatula in a small beaker. The paste was then placed into two syringes whose tip had been previously cut off. The setting time was measured using a so-called penetrometer [10]. All experiments were performed at 23 ± 2°C. Fifteen minutes after setting, the samples were placed into 10 ml of PBS solution at 37°C. As how long the hydration of the α-TCP powder would take was not known in advance, half of the samples were incubated for 1 day, whereas the other half was incubated for 2 days. After incubation, the samples were taken out and dried in air at 37°C. One day later, the samples were dried at 110°C until a constant weight was reached. The samples were then turned mechanically to flatten the top and bottom part of the cylindrical samples, and characterized by measuring the apparent density, the diametral tensile strength, the crystalline composition via XRD, and the specific surface area (BET). The α-TCP powder ground for 60 min was used for all experiments but those made to assess the effect of the amount of mixing liquid. In that case, the α-TCP powder that was ground for 15 min was taken. All these experiments were performed with a fixed phosphate concentration (0.2 M).

2.3. Characterizations

To measure the apparent density, the samples were first impregnated in isopropanol under vacuum (Epovac, Struers, Denmark). Then, the apparent volume was determined by measuring the volume of isopropanol displaced by the soaked sample (Archimedes Principle) [10]. The apparent density was obtained by dividing the weight of the sample by its apparent volume. An attempt was made to determine the sample porosity using this technique. In other words, the volume of isopropanol absorbed by the sample was measured and divided by its apparent volume [10]. As the porosities measured with this method were much smaller than those that could be calculated, it was concluded that this method was not suitable for the present cements. Two explanations were proposed: (i) not all the pores were open and/or (ii) the pores were so small that the impregnation took either very long (at 10 kPa) or required a very powerful vacuum. After these measurements, the samples were dried in air at room temperature and then at 110°C until a constant weight was reached. Afterwards, the samples were kept at 0% humidity (silica gel). The diametral tensile strength of the dried cement samples (diameter 12.5 mm, length 8–12.5 mm) was measured at a cross-head speed of 0.5 mm/min (Zwick UPM 1475, Ulm, Germany). The specific surface area of the dried samples was measured using nitrogen adsorption and applying the BET theory (Gemini 2360, Micromeritics, USA). The cement samples were initially ground, but as no difference was measured between sample chunks and ground specimens, all further measurements were carried out using intact specimens. The weight of each specimen varied in the range of 0.2–0.7 g. For XRD measurements, the samples were ground by hand with a pestle and a mortar. The powder was packed in a cavity in an aluminum sample holder. The measurements were done on a Philips PW1800 X-ray powder diffractometer (XRD) using Ni-filtered Cu-Kα radiation (40 kV, 30 mA) and an automatic divergence slit. The investigation range was from 4 to 40° (2θ) with 1 s per step (0.02° 2θ).

2.4. Solubility calculations

The solubility calculations were performed using known solubility data [11]. To simplify the calculations, it was assumed that carbonate ions did not play a role.

3. Results

The CSD amount and the phosphate concentration had an effect on the cement setting time (Figs. 1 and 2). Clearly, the most important factor affecting the setting time was the phosphate concentration (Fig. 2): an increase of the latter concentration enabled a two-fold decrease of the setting time. However, this effect was modulated by the CSD amount (Fig. 1). At a low CSD amount, a large decrease of the cement setting time was observed at all phosphate concentrations. At a large CSD amount, an increase of the setting time was observed, but its position and intensity varied according to the phosphate concentration: a low phosphate concentration led to an early and rapid setting time increase, whereas a large phosphate concentration prevented any setting time increase (Fig. 1). These results suggest an interaction between the CSD amount and the phosphate concentration.

An increase of the amount of mixing liquid provoked an increase of the cement setting time (Fig. 3). As a comparison, the setting times obtained with 1.72 ml mixing liquid and the α-TCP powder ground for 15 and 60 min were 3.7 and 2.0 min with 0.37 g CSD, and 8.2 and 5.3 min with 0.74 g, respectively. This shows that a prolonged grinding leads to a decrease of the setting time.

The apparent density of the cement was observed to decrease with an increase of the CSD amount (Fig. 4). No significant difference could be found between the results obtained with 0.1 and 0.2 M phosphate concentration, or those obtained after 1 and 2 days of incubation. Despite a lack of significance (only two measurements), the apparent density of the samples obtained with 1.11 g CSD and 0.2 M phosphate concentration was markedly lower than those obtained with 0.1 M.

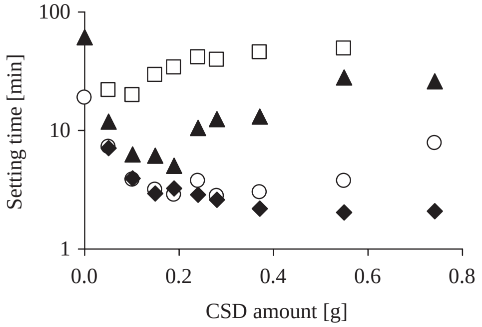

Fig. 1. Effect of the CSD amount on the cement setting time (logarithmic scale). Phosphate concentration: (□) 0.05 M; (▲) 0.10 M; (○) 0.20 M; and (◆) 0.30 M. Each point is an average of two measurements.

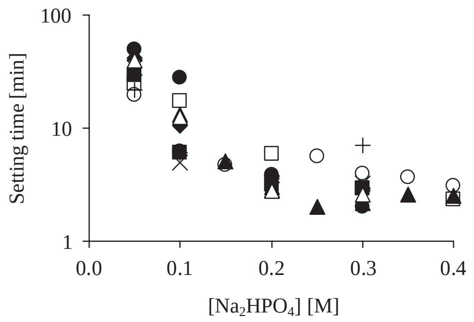

Fig. 2. Effect of the phosphate concentration on the cement setting time (logarithmic scale). CSD amount: (+) 0.05 g; (○) 0.10 g; (×) 0.19 g; (◆) 0.24 g; (△) 0.28 g; (▲) 0.37 g; and (●) 0.55 g; (□) 0.74 g. Each point is an average of two measurements.

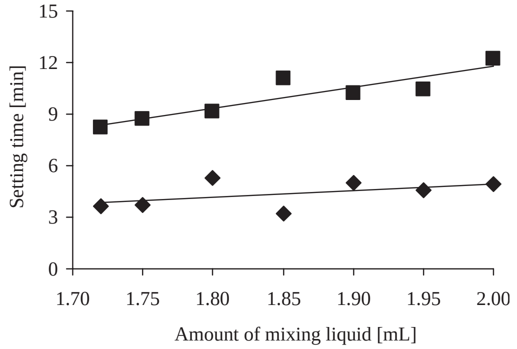

Fig. 3. Effect of the amount of mixing liquid on the setting time of α-TCP–CSD–water mixtures. $Na_2HPO_4 \cdot 2H_2O$ concentration: 0.2 M. Lower curve: 0.37 g CSD. Upper curve: 0.74 g CSD. α-TCP powder ground for 15 min.

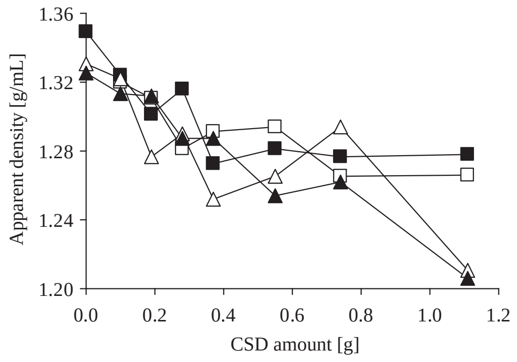

Fig. 4. Effect of the CSD amount, the incubation time and the phosphate concentration on the apparent density of the cement: (■) 0.1 M, 1 day; (▲) 0.2 M, 1 day; (□) 0.1 M, 2 days; and (△) 0.2 M, 2 days.

The diametral tensile strength of the cement was observed to be rather independent of the CSD amount, the incubation time, the phosphate concentration, and the amount of mixing liquid (Fig. 5). However, the standard deviation of the results was very high, which might have prevented the observation of a significant effect. In any case, if the CSD amount, the incubation time, the phosphate concentration, or the amount of mixing liquid had an effect, this effect would be small.

The specific surface area of the cement samples was increased by the addition of small amounts of CSD (Fig. 6a). However, hardly any changes were observed beyond 0.2 g CSD. An increase of the phosphate concentration from 0.1 to 0.2 M provoked a small but significant decrease of the specific surface area, but only after 1 day of incubation. Lower specific surface areas were measured for smaller (0.05 M) and larger (0.25, 0.30, 0.35 and 0.40 M) phosphate concentrations (not shown here). Interestingly, an increase of the incubation time led to a small decrease of the specific surface area. The specific surface area was slightly increased by an increase of the amount of mixing liquid, and a decrease of the amount of CSD (Fig. 6b).

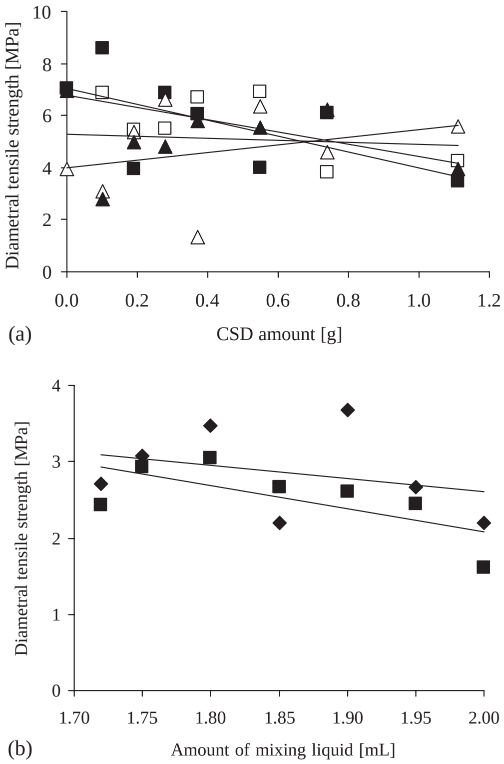

Fig. 5. Evolution of the diametral tensile strength of the cement (a) as a function of the CSD amount, the time of incubation and the phosphate concentration: (■) 0.1 M, 1 day; (▲) 0.2 M, 1 day; (□) 0.1 M, 2 days; and (△) 0.2 M, 2 days and (b) as a function of the CSD amount, and the amount of mixing liquid. Phosphate concentration: 0.2 M; (■) 0.37 g and (●) 0.74 g. The lines correspond to the regression lines of each data series.

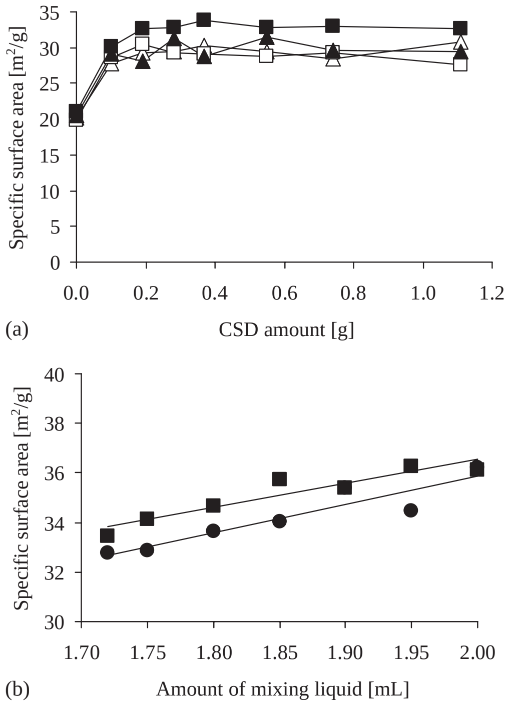

Fig. 6. Evolution of the specific surface area of the cement as a function of (a) the CSD amount, the time of incubation and the phosphate concentration: (■) 0.1 M, 1 day; (▲) 0.2 M, 1 day; (□) 0.1 M, 2 days; (△) 0.2 M, 2 days and (b) the CSD amount, and the amount of mixing liquid. Phosphate concentration: 0.2 M; (■) 0.37 g and (●) 0.74 g.

According to the XRD spectra, the cement samples contained a mixture of apatite, CSH and α-TCP (Fig. 7). A closer look at the peak intensities shows that the relative intensity of the CSH peak at $d = 0.601$ nm (close to 15° 2θ, 80% intensity; JCPDS File 41-224) was almost undetectable below 0.2 g CSD and then steadily increased. Simultaneously, the α-TCP peak rapidly increased with a small increase of the CSD amount and then remained stable or even slightly decreased (Fig. 8). Interestingly, the phosphate concentration had no significant effect on the CSH relative peak intensity, but had a large effect on that of α-TCP: a larger phosphate concentration led to larger α-TCP peaks. The results were similar at 2 days even though the α-TCP peaks were smaller. Another interesting observation is the fact that the 60% intensity peak of HA peak at $d = 0.2778$ nm (close to 32° 2θ, JCPDS file 9-432; see right arrow in Fig. 7) decreased with an increase of the CSD amount. A similar behavior was observed for the HA peaks at $d = 0.308$ and 0.317 nm (close to 28.5° 2θ, JCPDS file 9-432; see left arrow on Fig. 7).

Using solubility data [11,12], the solubility of HA, CDHA, CSD, and α-TCP was determined (Fig. 9). HA, CDHA and α-TCP have a solubility minimum at slightly basic pH values, whereas CSD has a constant value. So, at neutral pH values, CSD is about one and two orders

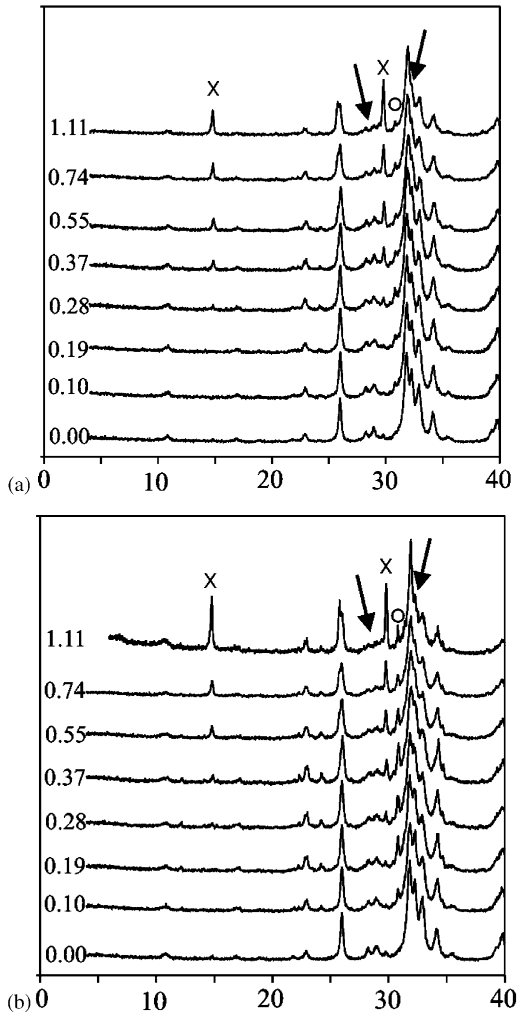

Fig. 7. XRD spectra of the cement samples as a function of CSD amount. Incubation time: 1 day. From bottom to top: CSD amount = 0.00, 0.10, 0.19, 0.28, 0.37, 0.55, 0.74 and 1.11 g. [$Na_2HPO_4 \cdot 2H_2O$] concentration: (a) 0.1 M and (b) 0.2 M. The most important peaks of CSH and α-TCP are indicated by (×) and (○), respectively. The largest peak corresponds to the main apatite peak. The arrows show some apatite diffraction peaks whose intensity varies with the CSD amount.

of magnitude more soluble than α-TCP and HA, respectively. Solubility data can also be used to determine the solubility of α-TCP in equilibrium with CSD (Fig. 9). The comparison of the solubility data of α-TCP in the absence and in the presence of CSD shows that α-TCP solubility is strongly reduced in the presence of CSD (Fig. 10). For example, the reduction is five-fold at pH 7 and 20-fold at pH 9.

An important aspect of the setting reaction is the supersaturation (SS) of the mixing liquid towards CDHA (see also in Discussion). This value is defined as

$$SS = \mathrm{Log}\left(\frac{(Ca^{2+})^9(PO_4^{3-})^5(HPO_4^-)(OH^-)}{K}\right), \tag{5}$$

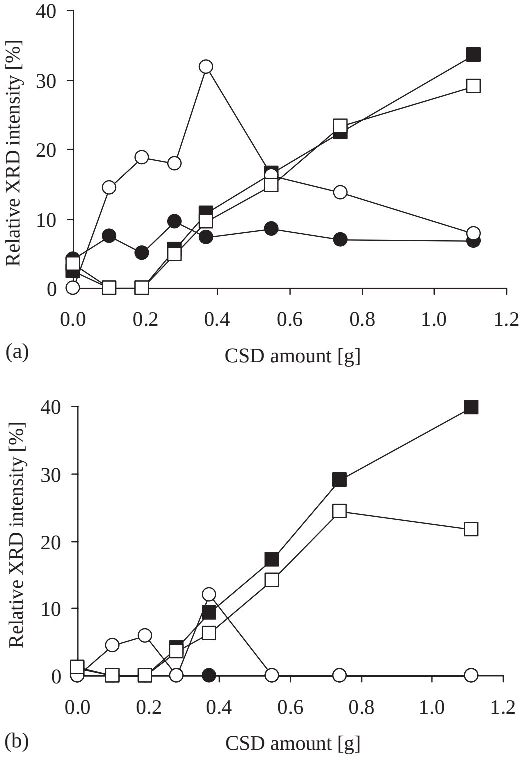

Fig. 8. Relative XRD intensity of α-TCP and CSH as a function of the CSD amount and the phosphate concentration. The relative intensity is expressed by the ratio between the intensity of the considered peak and the maximum diffraction peak (■) CSH, 0.1 M; (□) CSH, 0.2 M; (●) α-TCP, 0.1 M; (○) α-TCP, 0.2 M. (a) One day of incubation and (b) 2 days.

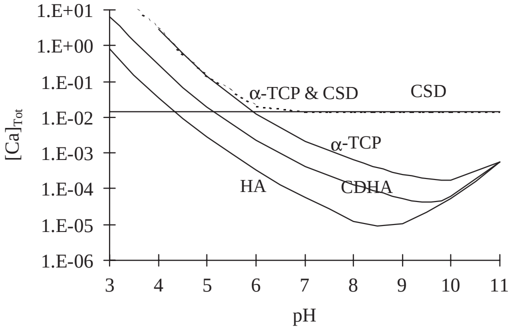

Fig. 9. Solubility isotherm of HA, CDHA, α-TCP, and CSD. The solubility is expressed as the total calcium concentration present in solution. The dashed line represents the solubility of α-TCP in equilibrium with CSD.

where (Ca^{2+}), (PO_4^{3-}), (HPO_4^-), and (OH^-) are the activities of the ions Ca^{2+}, PO_4^{3-}, HPO_4^- and OH^-, and K is the solubility constant of CDHA ($10^{-85.1}$, [12]). Using this definition, the saturation of CSD–Na_2HPO_4–water mixtures was determined as a function of pH and Na_2HPO_4 concentration (Fig. 11). At neutral pH values, the mixing solution was strongly supersaturated towards CDHA.

4. Discussion

Before discussing the results of the present study, a remark should be made concerning the setting time and the setting rate of the cement. The setting time of a cement corresponds generally to the onset of the setting reaction [13,14]. Therefore, the setting time depends on the initial setting rate of the cement. As the setting rate of the cement is not a constant value, but varies with time, a cement might have a short setting time, but might require a long time to reach 100% conversion of α-TCP into CDHA. For example, the setting time of commercial calcium phosphate cements is generally close to 10 min, whereas the setting reaction lasts typically several days.

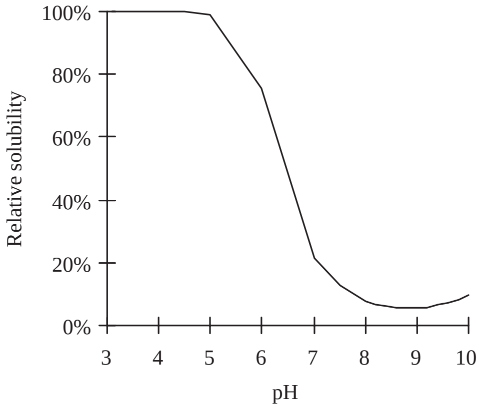

Fig. 10. Solubility of α-TCP in equilibrium with CSD. The solubility is given as the ratio between the solubility of α-TCP without CSD and with CSD. At pH 8–9, the solubility of α-TCP is reduced 20-fold by the presence of CSD.

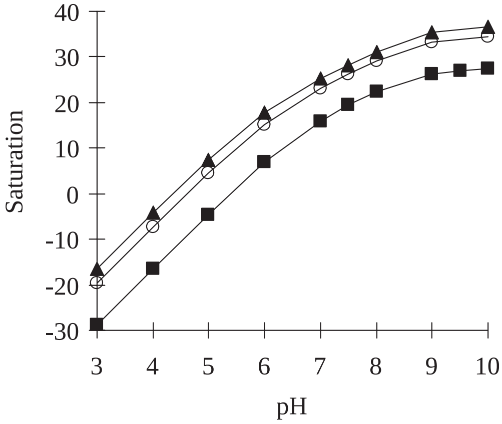

Fig. 11. Saturation of the mixing liquid towards CDHA precipitation. The mixing liquid is in equilibrium with CSD. Initial Na_2HPO_4 concentration in the mixing liquid: (■) 0.01 M; (○) 0.1 M; and (▲) 0.2 M.

4.1. Setting time

Various explanations can be proposed to explain the effect of CSD amount and phosphate concentration on the cement setting time. These explanations are summarized in Table 1. All these explanations are based on kinetics and solubility considerations. In order for CDHA crystals to precipitate, the solution has to be supersaturated. When α-TCP is mixed with water, the aqueous solution is initially undersaturated towards CDHA and α-TCP. Therefore, α-TCP starts dissolving. Solubility calculations show that when α-TCP–water mixtures have reached an equilibrium, the resulting solution has a pH close to 9.74 and is supersaturated towards CDHA (SS = 7.0). Therefore, at a certain point in the dissolution process, the mixing solution becomes supersaturated towards CDHA, and CDHA can start precipitating. CDHA precipitation eventually results in the entanglement of CDHA crystals, and hence to the hardening of the mixture. During setting, α-TCP is continuously dissolved and replaced by CDHA. The setting reaction stops when all α-TCP has been transformed into CDHA. As CDHA and α-TCP have almost the same composition, the setting reaction does not provoke a change of pH (Eq. (2)). So α-TCP–water mixtures are expected to set at a pH close to 9.74, where α-TCP has its lowest solubility.

The addition of chemicals such as Na_2HPO_4 and/or CSD powder is expected to modify the setting reaction.

Table 1
Possible factors that can affect the setting reaction of the cement

Explanation	Effect
1. CSD dissolution rapidly increases the supersaturation towards CDHA in the mixing liquid	The setting reaction starts earlier Setting time decreases
2. The dissolution of CSD increases the saturation of the mixing liquid towards α-TCP, hence decreasing α-TCP dissolution rate.	The setting reaction is slowed down Setting rate decreases
3. The presence of phosphate ions in the mixing solution increases its supersaturation towards CDHA.	The setting reaction starts earlier Setting time decreases
4. The presence of phosphate ions in the mixing solution increases the saturation of the mixing liquid towards α-TCP, hence decreasing α-TCP dissolution rate.	The setting reaction is slowed down Setting rate decreases
5. The phosphate ions of the mixing liquid react with calcium ions stemming from CSD dissolution to form CDHA. This reaction releases hydronium ions that accelerate the setting reaction.	The setting reaction starts earlier and is accelerated Setting rate increases Setting time decreases

Chemicals can modify the pH value of the setting reaction and/or modify the supersaturation of the solution towards CDHA precipitation. For example, at neutral and slightly basic pH values, CSD is more soluble than α-TCP and CDHA (Fig. 9). Therefore, the presence of CSD crystals in the cement should lead to a rapid increase of the concentration of dissolved calcium ions in the mixing liquid, and hence to a fast attainment of a supersaturation in the mixing liquid (towards CDHA). As a result, an increase of the initial setting rate should be measured. This explanation can be accounted for the decrease of setting time measured when CSD is added to the cement (Fig. 1). Obviously, this effect depends on the dissolution rate of CSD, which itself depends on the particle size distribution of CSD. Thus, a decrease of CSD particle size is expected to shift the curves "setting time = *f*(CSD amount)" to larger CSD values.

Similarly, the presence of phosphate ions in the mixing solution increases the initial supersaturation of the mixing solution towards CDHA and hence should increase the initial setting rate. This could explain the decrease of setting time observed with an increase of the phosphate concentration (Figs. 1 and 2). This effect has been previously reported by other authors in α-TCP–water mixtures [9].

As previously seen, the addition of CSD or phosphate ions into the mixing liquid is expected to accelerate the initial increase of the supersaturation of the mixing liquid towards CDHA precipitation (Fig. 11), hence accelerating the initial setting rate and decreasing the setting time. Simultaneously, the addition of CSD or phosphate ions into the mixing liquid increases the saturation of the mixing liquid towards α-TCP, hence provoking a decrease of the dissolution rate of α-TCP. The latter effect is expected to decrease the transformation rate of α-TCP into CDHA. Therefore, an increase of the CSD amount or the phosphate concentration should lead to an increase of the setting time and of the α-TCP fraction found after 1 day of incubation. Experimentally, the latter effect was found. Moreover, large CSD amounts provoked an increase of the setting time (Fig. 1). However, large phosphate concentrations did not provoke an increase of the setting time. It is possible that the phosphate concentrations used in this study were not large enough.

When CSD and phosphate ions are simultaneously present in the cement paste, CSD can precipitate with phosphate ions according to reaction (3). Assuming that all phosphate ions in solution react with CSD, the amount of CSD consumed by phosphate ions is 0.044 g for a 0.1 M phosphate concentration (or 0.178 g for 0.4 M). These values are much larger than the solubility of CSD (about 3 mg in a phosphate-free mixing solution). As a result of this precipitation, a decrease of setting time is expected. Reaction (3) also provokes the release of hydronium ions that can lower the pH values in the cement paste, hence increasing α-TCP solubility (Fig. 9). The latter phenomenon is expected to accelerate α-TCP dissolution, and the transformation of α-TCP into CDHA. Experimentally, low setting times are indeed observed at high CSD amounts and phosphate concentrations (Fig. 1). Additionally, the α-TCP fraction presents a maximum at an intermediate CSD amount (Fig. 8). Furthermore, pH measurements performed in diluted systems (4 g of powder for 40 ml of solution) have shown that the pH of the solution decreases with time (results not shown here). The decrease is stronger for larger CSD and phosphate concentrations. For example, the pH of a 0.2 M Na_2HPO_4 solution decreased from 9.0 to 8.2 with 0.37 g CSD (and 3.63 g α-TCP) and from 9.0 to 7.7 with 0.74 g CSD (and 3.26 g α-TCP).

The amount of mixing liquid had a relatively small effect on the setting time of the cement. This effect was observed for other calcium phosphate cements [15]. The increase of setting time is due to the dilution of the system.

4.2. Apparent density

The decrease of apparent density of the cement observed with an increase of the CSD amount (Fig. 4) is due to the fact that CSD is less dense than α-TCP. Therefore, the replacement of α-TCP with CSD must lead to an increase of cement volume (the powder and liquid weights are always constant) and hence a decrease of apparent density. If CSD is transformed into CDHA/HA (see reactions (1) and (2)), water molecules are released leading to an additional decrease of the apparent density. Knowing the chemical reactions involved during setting (conversion of α-TCP and CSD into CDHA), the apparent density of the cement can be calculated. The comparison of the calculated and measured data shows a very good correlation for the apparent density (Fig. 12). The measured values are just a little bit higher than the calculated values.

4.3. Diametral tensile strength

The diametral tensile strength of the cement was observed to be rather independent of the CSD amount, the phosphate concentration, and the amount of mixing liquid (Fig. 3). However, the standard deviation of the results was very high, which might have prevented the observation of a significant effect. In any case, if the CSD amount, the amount of mixing liquid, or the phosphate concentration had an effect, this effect would be small. Based on the specific surface area measurements, an increase of the mechanical properties was in fact expected to be up to about 0.2 g CSD. It is indeed well known that a finer microstructure leads to larger

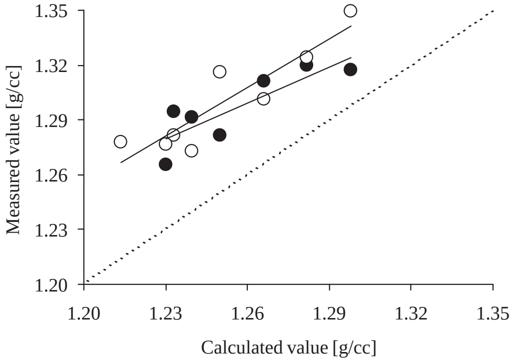

Fig. 12. Comparison between calculated and measured apparent density. Phosphate concentration: 0.1 M. Incubation time: (○) 1 day and (●) 2 days.

mechanical properties. A decrease of the diametral tensile strength was expected with an increase of the amount of mixing liquid due to an increase of the cement porosity (Fig. 5b). The tensile strength results show this trend, but the decrease was not very significant. The difference observed between the various cement samples (compare Figs. 5a and b) is still unclear. It could stem from the difference of α-TCP powder, as the α-TCP powder used to investigate the effect of mixing liquid had a lower specific surface area (1.07 ± 0.03 against $1.84 \pm 0.07\,m^2/g$).

4.4. Crystalline composition

The various XRD patterns show that the cement samples contained HA, CSH (bassanite), and remnants of α-TCP. The presence of CSH is surprising as no CSH was added to the cement. One possibility could be a transformation of the cement during drying (at 110°C). However, CSD is supposed to be stable up to 128°C [16]. Therefore, a differential scanning calorimetry (DSC) scan was performed. Results showed that CSD started loosing bound water below 100°C and had almost lost all water below 110°C. The effect of the transformation of CSD into CSH on the physico-chemical properties of the cement is unknown. Additional experiments are probably required to determine these effects.

The comparison of the cement setting times and crystallographic composition (Figs. 1, 7, and 8) shows that CSD and phosphate ions had an ambivalent effect: an increase of the CSD amount and phosphate ions provoked a decrease in the cement setting time but an increase in the α-TCP fraction at 1 day. Therefore, CSD and phosphate ions provoked an initial increase of the setting rate, leading to a shorter setting time, and a long-term decrease of the setting rate, leading to a longer setting reaction. Looking at the literature, Ginebra et al. [9] observed similar results as those presented here, i.e. the addition of phosphate ions to α-TCP–water mixtures was observed to have a much stronger effect on the initial setting time of α-TCP–water mixtures than on their final setting time, suggesting that the initial part of the setting reaction was accelerated and the final part was slowed down.

Almost no CSH could be detected by XRD below 0.2 g CSD (Fig. 8). Above that value, there was a constant increase of the relative intensity of CSH, suggesting a constant increase of the CSH (and hence CSD) amount. This is normal since there was a constant increase of the CSD amount in the initial cement composition. The absence of CSH in the XRD spectra when the cement samples contained less than 0.2 g CSD in the initial composition could be due to the dissolution of CSD and/or its reaction with the phosphate ions present in the mixing solution (see above).

The amount of 0.2 g CSD seemed to play a very important role for the cement microstructure. Below this value, a rapid increase of the specific surface area was measured (Fig. 6a). Above that value, the specific surface area was almost constant. This suggests that CSD crystals accelerated the nucleation of CDHA crystals below 0.2 g CSD. The reason why the change would occur at 0.2 g CSD is unclear. The XRD data also show that the diffraction peaks corresponding to the (1 1 2), (1 0 2) and (2 1 0) planes of CDHA almost disappeared with an increase of the CSD amount, suggesting that CSD had in fact an effect on the growth of CDHA crystals. The reason why there would be almost no difference of specific surface area as a function of the CSD amount is unclear. A decrease would be expected because CSD has a much lower specific surface area than the precipitated apatite (a value of $4\,m^2/g$ was measured for the CSD powder). This discrepancy could be due to the fact that an increase of the CSD amount constantly decreased the average CDHA crystal size, hence compensating the decrease of surface due to the decrease of the CDHA fraction in the cement.

A decrease of the specific surface area with an increase of the incubation time (Fig. 7) can be expected since small crystals are thermodynamically less stable than large crystals (Ostwald ripening): small crystals are dissolved, whereas large crystals grow. This phenomenon was only observed with a 0.1 M phosphate concentration. With a 0.2 M phosphate concentration, no significant change was detected. However, between day 1 and 2 there was a strong decrease of the α-TCP amount that should have led to a net increase of the specific surface area. Therefore, it can be concluded that for both phosphate concentrations, there was an increase of the average particle size with an increase of the incubation time. The measured values ($19–34\,m^2/g$) were similar to that found by TenHuisen and Brown [17] when hydrolyzing α-TCP in water ($22–23\,m^2/g$).

5. Conclusion

The addition of CSD powder to α-TCP–water cement mixtures strongly decreased their setting time, particularly when the phosphate concentration was high. Simultaneously, there was an increase in unreacted α-TCP fraction after 1 day of incubation, indicating that the end of the setting reaction was slowed down. These results could be explained based on solubility considerations. The presence of a fast-releasing calcium salt (CSD) or phosphate ions in the initial cement paste decreased the time required for the cement paste to become supersaturated towards CDHA, hence leading to a shorter setting time. Parallel to this effect, there was an increase of the saturation of the mixing liquid towards α-TCP, hence slowing down α-TCP dissolution and α-TCP transformation into CDHA. This could explain the increase of unreacted α-TCP fraction seen after 1 day of incubation. When large amounts of CSD and phosphate ions were simultaneously present, CSD could react with the phosphate ions to form CDHA, hence releasing hydronium ions that accelerated the setting reaction. Therefore, the effect of CSD depended on the amount of phosphate ions in the solution and vice versa. In conclusion, CSD and phosphate can be used to control the setting time of α-TCP–water mixtures, without markedly modifying the diametral tensile strength of the resulting hardened cement.

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