Wet or dry mechanochemical synthesis of calcium phosphates? Influence of the water content on DCPD–CaO reaction kinetics

H. El Briak-BenAbdeslam, M.P. Ginebra, M. Vert, P. Boudeville

Institut des Biomolécules Max Mousseron, Dpt Biopolymères Artificiels, IBMM UMR-CNRS 5247, Faculté de Pharmacie, 15 Avenue Charles Flahault, BP 14 491, 34093 Montpellier Cedex 5, France

Research Centre in Biomedical Engineering, Biomaterials Division, Department of Materials Science and Metallurgy, Technological University of Catalonia (UPC), Avda. Diagonal 647, E-08028 Barcelona, Spain

Abstract

Mechanosynthesis of calcium phosphates can be performed under wet or dry conditions. In most papers and patents, grinding under wet conditions was selected. So far, only a few papers were devoted to dry mechanosynthesis of calcium phosphates. To understand why wet mechanosynthesis was preferred, the influence of water addition on the kinetics of the mechanochemical reaction of dicalcium phosphate dihydrate with calcium oxide was investigated. The DCPD disappearance rate constant $k$ and the final reaction time $t_f$ were determined in each case and correlated with the water content present in the slurry. Results showed that the addition water (i) slowed down the reaction rate and (ii) increased the powder contamination by mill material (hard porcelain) due to ball and vial erosion; and that (iii) wet milling did not generate the expected products, in contrast to dry grinding, because porcelain induced hydroxyapatite decomposition with the formation of $\beta$-tricalcium phosphate and silicon-stabilized tricalcium phosphate. Consequently, dry mechanosynthesis appears preferable to wet milling in the preparation of calcium phosphates of biological interest.

© 2007 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Mechanosynthesis; Calcium phosphates; Water content; Kinetics study; Planetary ball mill

1. Introduction

A number of bone substitutes have been developed as alternatives to autogenous and allogenous bone grafts. Among these synthetic biomaterials, calcium phosphate ceramics have been used successfully in orthopedics, dentistry and maxillofacial surgery [1–4]. Such ceramics are composed either of pure $\beta$-tricalcium phosphate ($\beta$-TCP) with a 1.5 calcium-to-phosphate (Ca/P) ratio or of stoichiometric hydroxyapatite (HA) with Ca/P = 1.67, or of a mixture of $\beta$-TCP and HA (biphasic calcium phosphate ceramic BCP) with $1.5 < \text{Ca/P} < 1.67$. These ceramics are generally prepared either by a solid-state reaction at high temperature between a calcium salt and a phosphate salt or by heating a poorly crystallized hydroxyapatite or calcium-deficient hydroxyapatite (CDHA) obtained by solution precipitation [5–7].

Mechanosynthesis [8,9] is an alternative route to produce HA or CDHA during which the reaction is activated by mechanical milling. In a mill, the reactants are crushed between balls or ball and wall (horizontal or planetary ball mill, attritor, vibratory ball mill), or between rings or ring and wall (multi-ring media mill). Reagents absorb part of the energy provided by the collisions or frictions that provide the energy necessary for the reaction. Mechanosynthesis can be performed under wet or dry conditions. Wet mechanosynthesis consists in grinding an aqueous suspension of the starting materials (wet attrition or the mechanochemical–hydrothermal method) with a liquid-to-powder ratio ranging generally from 60 to 95 wt.%.
mechanosynthesis, reagent powders are directly ground without any solvent. In most papers and patents concerning mechanosynthesis of calcium phosphates, grinding was performed under wet conditions [10–24]. Beside our own works [25–30], only a few papers have been devoted to dry mechanosynthesis of calcium phosphates [31–34]. It has been shown that (i) the dry grinding of any acid calcium phosphate with any basic calcium phosphate or CaO, Ca(OH)$_2$ and CaCO$_3$ leads to calcium phosphates [31–34]. Dicalcium phosphate dihydrate (DCPD) is important to understand why wet mechanosynthesis has been in preference to prepare calcium phosphates, we investigated the influence of the addition of water on the kinetic constants of the mechanochanical reaction of dicalcium phosphate dihydrate (DCPD) with calcium oxide.

2. Materials and methods

2.1. Chemicals

Chemicals of analytical reagent grade were purchased from Aldrich (HA, CaO, ascorbic acid), Fluor (DCPD), Riedel-de-Haën (Acetone), Prolabo (La$_2$O$_3$), Merck (CaCO$_3$, H$_2$SO$_4$ 96%, ammonium heptamolybdate tetrahydrate), Labosi (H$_3$PO$_4$ 85%) and Carlo-Erba (HCl 37%). Commercial CaO was heated at 900 °C for 2 h to remove H$_2$O and CO$_2$ and stored in vacuum desiccators. The CaO median particle size $d_{50}$ was around 7 μm ($d_{10}$–$d_{90}$ = 2–40 μm; calculated specific surface area = 4.3 m$^2$ g$^{-1}$, Mastersizer, Malvern Instruments). DCPD was used as received. Its median particle size was 8 μm (1.6–27 μm; calculated specific surface area, 3.5 m$^2$ g$^{-1}$). Water was first deionized on an ion exchange resin before bi-distillation in a quartz apparatus.

2.2. Materials

The planetary ball mill was a Retsch Instrument with a porcelain vial (500 ml, radius: 5 cm) and porcelain balls (mean diameter: 2.5 cm; mean weight: 24 g; and mean surface area: 20 cm$^2$). The vial eccentricity on the rotating disc was 3.65 cm. Vial and disc rotation speeds were opposite and equal.

X-ray diffraction (XRD) patterns were recorded on an Automatic diffractometer composed of a Philips PW3830 HT generator, a horizontal goniometer (CGR) and X-ray tube Philips 2273/20 using a Cu anti-cathode (Ka$_1$ 1.5405 Å) with a nickel filter followed by a quartz monochromator. Differential scanning calorimetry (DSC) analyses were carried out with a Perkin–Elmer DSC 6 differential scanning calorimeter using indium and zinc as calorimetric and thermometric references. Infrared absorption spectra were recorded on a FTIR Perkin–Elmer Spectrum One (ATR system) in the 4000–400 cm$^{-1}$ range. Calcium concentrations were determined by atomic absorption spectrometry (Perkin–Elmer AA300) using an air–acetylene flame, with 0.1% w/v lanthanum chloride (La$_2$O$_3$ + HCl) as spectral buffer and standards prepared from CaCO$_3$ + HCl in the range 0–25 ppm. Phosphate concentrations were determined by molecular absorption spectrophotometry (Beckman Model 24, double beam) in the state of phosphomolybdate complex reduced by ascorbic acid ($\lambda$ = 660 nm) [35] with standards prepared from standardized H$_3$PO$_4$ solution in the range 0–30 ppm.

2.3. General grinding procedure

Dicalcium phosphate dihydrate and calcium oxide, each carefully measured to obtain 15 g mixtures with the desired theoretical (1.50, 1.60, 1.67) Ca/P ratio, were placed in the 500 ml vial with five balls. Then, no water (dry mechanosynthesis) or 5, 10, 15, 30, 50 or 100 ml of water was added to the powder (wet mechanosynthesis). The dry powder or the slurries were ground using a rotation speed of 350 rpm and with no change in the rotation direction until the reaction was achieved.

Because kinetics parameters depend linearly on the product of the total mass by the total surface area of the balls [28], the ball mass and diameter were regularly measured accurately after drying at 110 °C for 1 h. All results were then normalized for a 119 g total mass and a 98.5 cm$^2$ total surface area.

2.4. Powder evolution

At different intervals, depending of the transformation rate, 50–100 mg of powder or 0.2–1 ml of slurry was taken for XRD or DSC analysis in order to determine the reaction kinetics and to evaluate the changes in the powder composition. Slurry samples were first filtered under vacuum (porosity 4 sintered glass filter) then washed with acetone to remove water and stop any continuation of the reaction occurring similar to calcium phosphate cement setting. Samples obtained by dry mechanosynthesis were also washed with acetone, because of the presence of the small amount of water (5–15 wt.%) generated from the DCPD–CaO reaction [27] (Eq. (1)):

$$6\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} + 4\text{CaO} \rightarrow \text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 + 14\text{H}_2\text{O}$$

(1)

The relative amount of DCPD in the powder at each interval was determined either by XRD (area of a DCPD diffraction peak) or by DSC (enthalpy of the endotherm corresponding to the dehydration of DCPD) [27,36]. By XRD, the area of the DCPD X-ray diffraction peak at 2θ = 11.60° (plane 0 2 0) was calculated on patterns.
recorded from $2\theta = 10–13$ with 0.02° $2\theta$ increments (20 acquisitions, acquisition delay of 500 ms) after baseline subtraction. By DSC, all experiments were performed on 3–4 mg samples in aluminum pans with a 20 °C min$^{-1}$ heating rate. The enthalpy (expressed in J g$^{-1}$) of the DCPD endothermic peak at 170–210 °C was determined from thermograms recorded from 50 to 250 °C [27]. The DCPD disappearance rate constant was determined by plotting the natural logarithm of the DCPD content vs. the grinding time [27]. The slope of the straight line obtained represented the rate constant $k$ expressed in h$^{-1}$.

In a previous work [27], it was shown that, for a starting powder with Ca/P > 1.5, the total DCPD consumption did not indicate the end of the reaction, but that additional time was required, which increased exponentially with the Ca/P ratio. This extra time was necessary to consume all the CaO (or Ca(OH)$_2$) and complete the reaction. Therefore, the final reaction time ($t_f$) was determined by a phenolphthalein test ($\varphi\varphi$ test) that indicated when the calcium oxide or calcium hydroxide was exhausted (no powder pink coloration) [27].

Suspensions were then filtered, washed with acetone, dried at 60 °C for 3 h and heated at 950 °C for 2 h to determine the powder composition by XRD [5,26].

### 3. Results

#### 3.1. DCPD determination using XRD and DSC

DCPD, DCPA, HA, CaO and Ca(OH)$_2$ powders were analyzed by DSC in the 50–250 °C range. An endothermic peak was present on the DCPD thermogram only, thus indicating there was no possible interference between DCPD and other products that could be associated during the mechanochemical process. To check the quality of the DCPD content determination in the powder after different grinding times, DCPD–CDHA (Ca/P 1.5) mixtures were prepared with different amounts of DCPD (0–100 wt.% ) and analyzed by both XRD and DSC. The experimental DCPD content (in g g$^{-1}$) in the different mixtures was calculated from the surface area of the DCPD diffraction peak at $2\theta = 11.60$° (XRD) or from the enthalpy of the DCPD dehydration endothermic peak (DSC) of pure DCPD. These experimental DCPD contents were plotted against the theoretical DCPD contents. An excellent linear variation was obtained regardless of the two methods (Eq. (2), XRD and Eq. (3), DSC):

$$\text{DCPD}_{\text{exp}} = 1.012 \text{DCPD}_{\text{theo}} - 0.005 \quad (r = 0.9998)$$  (2)

$$\text{DCPD}_{\text{exp}} = 0.998 \text{DCPD}_{\text{theo}} + 0.006 \quad (r = 0.9996)$$  (3)

#### 3.2. Influence of water addition on DCPD disappearance and on the final reaction time $t_f$

![Fig. 1. Variations in ln(DCPD) with the grinding time and with the amount of water added to 15 g of powder with Ca/P = 1.67.](image)

Fig. 1 shows the variations of ln(DCPD) with the grinding time for no added water (dry mechanosynthesis) and in the presence of 15 and 50 ml of water added to 15 g of powder. ln(DCPD) varies linearly with the grinding time in the presence of water, whatever the water amount and the Ca/P ratio as observed under dry conditions (Fig. 1, plot 0 ml and Ref. [27]). The slope of each ln(DCPD) = $f(t)$ plot corresponded to the DCPD disappearance rate constant $k$ expressed in h$^{-1}$. Values are given in Table 1. In the presence of water, the DCPD disappearance rate constant is independent of the Ca/P ratio as observed under dry conditions (Table 1, columns 0% and 50% water).

The time for complete reaction (final reaction time $t_f$) was determined by the $\varphi\varphi$ test. Data are given in Table 1, except for the cases, where 50 and 100 ml water was added. For these two last cases, the reaction had not completed after 48 h and $t_f$ could not be determined (nd). In the presence of 15 ml water (i.e. 50% water content), the final reaction time $t_f$ was plotted against the Ca/P ratio and compared with the corresponding results obtained without water addition (Fig. 2). Under the wet conditions, $t_f$ increased exponentially with the Ca/P ratio, as already observed in the case of dry mechanosynthesis [27].

#### 3.3. Powder composition after grinding

After complete reaction (negative $\varphi\varphi$ test), dried ground powders were analyzed by XRD. Whatever the amount of added water and the Ca/P ratio in the starting materials, XRD patterns showed profiles typical of an apatite with a low crystallinity. After heating at 950 °C for 2 h to determine the exact powder composition [5,26], the XRD pattern profiles varied with the Ca/P ratio as expected but, surprisingly, also with the percentage of water in the slurry (Figs. 3–5).

For Ca/P = 1.50, pure $\beta$-TCP was obtained by both dry and wet mechanosynthesis as expected (Fig. 3). In contrast, for Ca/P = 1.60 (Fig. 4), wet and dry grinding did not give the same final product. Under the dry condition, the final powder corresponded to a 60/40 wt.% HA/$\beta$-TCP mixture according to the surface areas of the main diffraction peaks of HA (plane 2.1.1 at $2\theta = 31.78$°) and of $\beta$-TCP (plane 0.2.10 at $2\theta = 30.90$°) [26]. Under the wet condition (water content 50 wt.%), $\beta$-TCP was the main final product, with a
small amount of HA (Fig. 4). For Ca/P = 1.67 (Fig. 5), the height of the HA main peak decreased with the amount of water and, in parallel, the $\beta$-TCP main peak increased. From 10 ml of added water, a new phase appeared, with a main XRD peak at $2\theta = 30.72^\circ$, which could correspond to $\alpha$-TCP (plane 0.3.4). Given the 950 °C temperature, i.e. below the $\beta$ to $\alpha$-TCP transition temperature (1150–1200 °C [6]), the appearance of $\alpha$-TCP was unexpected.

Although the theoretical Ca/P ratio was 1.67 in the starting materials, the XRD pattern of the wet mechano-synthesized powders seemed to correspond to a heated powder with a Ca/P ratio lower than 1.67, since it contained both HA and $\beta$-TCP. The greater the amounts of added water, the lower the amount of HA, suggesting a lower Ca/P ratio; a possible explanation could be that calcium ions remained dissolved in water and were eliminated.

<table>
<thead>
<tr>
<th>Water added (ml)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>30</th>
<th>50</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (wt.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca/P</td>
<td>1.50</td>
<td>1.60</td>
<td>1.67</td>
<td>1.67</td>
<td>1.67</td>
<td>1.67</td>
<td>1.67</td>
</tr>
<tr>
<td>$k$ (h$^{-1}$)</td>
<td>1.65</td>
<td>1.68</td>
<td>1.51</td>
<td>0.28</td>
<td>0.95</td>
<td>0.72</td>
<td>0.70</td>
</tr>
<tr>
<td>$t_f$ (h)</td>
<td>2.6</td>
<td>3.8</td>
<td>10</td>
<td>18</td>
<td>12</td>
<td>5</td>
<td>7</td>
</tr>
</tbody>
</table>

nd : not determined ($t_f > 48$ h); experimental errors<10% of the values.
during filtration. To verify this hypothesis, experiments with 15 and 30 ml of water for 15 g of powder were duplicated. After complete reaction, filtrates were collected and, after further washing with acetone and drying, the as-ground powders were dissolved with concentrated HCl (final pH 1). Calcium and phosphate contents in the filtrate and in the dissolved ground powder were determined by atomic absorption and ultraviolet–visible spectrophotometry, respectively. Whatever the amount of water added during the mechanochemical process, calcium was not detectable in the filtrates and phosphate was at the detection threshold. In the washed as-ground powders, the Ca/P ratio was 1.67 ± 0.02.

Infrared spectra of the washed as-ground powders were also recorded. These spectra indicated the presence of a very small amount of carbonate group replacing the phosphate group (CO$_3$ bands at 1465, 1410 and 874 cm$^{-1}$). This slight carbonation was undoubtedly due to CO$_2$ uptake during the regular opening of the vial to take powder samples for kinetics measurements.

During the dissolution of the washed as-ground powders by adding concentrated HCl to analyze the calcium and phosphate ions, the solution remained slightly turbid, even at pH 1, and the opalescence seemed to increase with the amount of water added during wet mechano synthesis. Thus, in a new set of experiments, 1 g of powder, obtained for the different percentages of water tested, was introduced into accurately weighed centrifugation tubes. The powders were dissolved with 4 ml of concentrated HCl. Suspensions were centrifuged (5000 rpm, 30 min) and then decanted. The remaining solid phase was washed with 1 ml deionized water, centrifuged, decanted and dried at 80°C for 3 h. Tubes with insoluble residues at pH 1 were accurately weighed and the mass of these residues was calculated. XRD analysis (Fig. 6) indicated that this insoluble residue was not a calcium phosphate, but was porcelain from the erosion of the balls and vial during milling. Because, for each water volume added, the grinding time to complete the reaction was different (Table 1), the masses of pollutant were normalized by expressing them in milligrams of pollutant per gram of powder and per hour of grinding (mg g$^{-1}$ h$^{-1}$). The specific hourly degree of pollution was plotted against the percentage of water in the slurry (Fig. 7). It varies linearly with the water percentage (Eq. (4)):

$$\text{Specific pollution} = 0.134 \times \text{water}\% - 3.2 \quad (r = 0.965)$$

Finally, despite the fact that all the washed as-ground powders gave a negative $\varphi\varphi$ test, after heating at 950°C, powders with an initial 1.67 Ca/P ratio, ground in the presence of more than 25 wt.% water, gave a positive $\varphi\varphi$ test, indicating the presence of a basic compound, while the $\varphi\varphi$ test remained negative for heated powders ground under the dry condition.

4. Discussion

4.1. Mechanism of the mechanochemical reaction in the presence of water

The following observations were made during the wet mechanochemical process whatever the percentage of water in the slurry:

(i) The linear variation of the natural logarithm of the DCPD content with the grinding time allows the calculation of the DCPD disappearance rate constant $k$ (Fig. 1);

(ii) This rate constant is independent of the Ca/P ratio for a given water percentage (Table 1, columns 0 and 15 ml of water); and

(iii) The final reaction time $t_f$ increased exponentially with the Ca/P ratio over 1.5 (Fig. 2).

Given these observations, it can be concluded that the mechanochemical reaction of DCPD with CaO (or Ca(OH)$_2$) followed the same mechanism in the presence...
of water as without any water addition, as previously proposed [27]. The reaction took place in two well-differentiated successive stages. In the first stage, DCPD reacted with CaO and first led to an amorphous calcium phosphate (ACP) that transformed into calcium-deficient hydroxyapatite with a Ca/P ratio of 1.5 (CDHA1.5) when DCPD was exhausted. The reaction had consumed 3 CaO (or 3 Ca(OH)$_2$) for 6 DCPD (Eq. (5)). When the starting materials had a Ca/P ratio of 1.5, the reaction was achieved according to Eq. (5):

$$6\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} + 3\text{CaO} (\text{or } \text{Ca(OH)}_2) \rightarrow \text{Ca}_9(\text{HPO}_4)_3(\text{OH}) + 14(\text{or}17)\text{H}_2\text{O} \quad (5)$$

In the second stage, and for Ca/P > 1.5 in the initial mixture (more than 3 CaO for 6 DCPD), CaO in excess was totally hydrated to Ca(OH)$_2$ by the added water or by the water produced by the reaction during the first stage. Ca(OH)$_2$ then reacted with CDHA1.5 to yield a CDHA in which the Ca/P ratio increased up to the value expected by the initial mixture composition (Eq. (6)). The longer the reaction time, the nearer to 1.67 the Ca/P ratio. The reaction was then:

$$\text{Ca}_9(\text{HPO}_4)_3(\text{OH}) + x\text{Ca(OH)}_2 \rightarrow \text{Ca}_{9-x}(\text{HPO}_4)_{3-x}(\text{OH})_{1-x} + x\text{H}_2\text{O}$$

$$(0 < x \leq 1) \quad (6)$$

### 4.2. Variation of $k$ and $t_f$ with the water present in the slurry

The presence of water during the mechanochemical process decreased the DCPD disappearance rate constant $k$ (or increased the time for complete DCPD disappearance) (Table 1 and Fig. 1). It also increased the final reaction time $t_f$ (Table 1 and Fig. 2). Thus, the presence of water slowed down the reaction rate. This decrease was not a continuous function, as shown by the anomalous values obtained for the 25% point (Table 1; 5 ml of water added to 15 g of powder). This can be explained by the small amount of water added to the powder creating a sticky paste instead of a slurry, which hindered the balls and caused the mechanochemical process to be less effective.

### 4.3. Variation of the ground powder composition with the water percentage in the slurry

Because (i) calcium ions were not found in the filtrates and (ii) the Ca/P ratio in the powders was 1.67–1.70 after filtration of the slurries, the presence of $\alpha$- and $\beta$-TCP in the powder obtained by wet mechano-synthesis could not be due to the formation of calcium-deficient hydroxyapatite as we first thought. IR spectra showed the presence of a carbonate group albeit in a very small amount. The heating of a B-type carbonated apatite led to a mixture of HA and CaO. The presence of this last compound could explain the basicity of the powder after firing (positive $\phi\phi$ test), but not the presence of $\alpha$- and $\beta$-TCP, which became predominant for a water percentage in the slurry of over 25%, although the carbonate content remained very low.

Increasing the water content in the slurry, both the transformation with heating of HA into $\alpha$- and $\beta$-TCP and the strong increase in powder pollution by the mill material were observed. These two features could be linked. To check this hypothesis, 1 g of HA (Ca/P = 1.67) obtained by dry mechano-synthesis and 1 g of a commercial HA (Aldrich, prepared by precipitation) were heated at 950 and 1100 °C for 2 h in the presence of 0.25 g of powdered mill material. This amount corresponded to the mean pollution (20 wt.%) observed in powder obtained by grinding 15 g of starting materials with 30 ml of water (67% water). XRD patterns of the heated HA without and with pollutant are given in Fig. 8. Without the addition of pollutant, mainly hydroxyapatite was obtained at both 950 and 1100 °C. The presence of a small amount of $\beta$-TCP within the HA has been explained previously [27]. It is due to the slight deficit of hydration water in DCPD (1.8 mol of water instead of 2). It is thus necessary to take a theoretical 1.7 Ca/P ratio in the starting material into account to obtain an actual 1.67 Ca/P ratio in the final product [27,37]. By heating in the presence of powdered mill material, HA was transformed into $\alpha$- and $\beta$-TCP (around 50% at 950 °C), the transformation being almost complete at 1100 °C. A similar behavior was observed by heating commercial HA in the presence of mill material. Thus, we can conclude that the evolution in the XRD pattern profiles of the heated powders with the water percentage in the slurry was due to an increase in pollution by the mill material.

Decomposition of HA was reported by Langstaff et al. [38] during the preparation of thin films of HA on quartz at 1000 °C and by heating a mixture of HA and tetrapropyl...
or tetraethyl orthosilicate. These authors observed a silica-dependent transformation of HA into β-TCP and α-TCP-like products. They explained this conversion by the fact that, under low water partial pressure, HA could decompose into β-TCP and CaO below 1100 °C, and that CaO reacted with silica to give calcium silicate, which then could react with HA or β-TCP to yield a new phase (Eq. (7)) that presented a crystalline structure similar to that of α-TCP.

Considering the 800–1000 °C temperature range of appearance of this phase, i.e. below the β to α-TCP transition temperature (1180 °C), and after analysis by different techniques, the authors called this new phase “silicon-stabilized tricalcium phosphate” (Si–TCP), in which SiO4 groups partially substitute for PO4 groups.

\[
\text{HA or } \beta\text{-TCP } + \text{CaSiO}_3 \rightarrow \text{Si–TCP} \tag{7}
\]

The mill used in our work was made of hard porcelain, a complex aluminum silicate with an excess of silica. The presence of SiO2 (or silicate) in the mill material was the probable cause of decomposition of HA in the same way as in Langstaff’s experiments. Our results are consistent with the appearance of an Si–TCP phase with an α-TCP-like structure and, because this compound was well studied and described in the discussion section of the Langstaff’s article [38], we did investigate the phenomenon further.

Langstaff et al. also demonstrated that HA decomposition was dependent on the silicon content (see Fig. 10 of Ref. [38]) and that transformation reached an equilibrium at a 0.75–1 molar fraction Si/HA. This explained the observed regular evolution of XRD patterns with the water percentage (Fig. 5) well because the powder pollution by the mill material increased with the water percentage in the slurry (Fig. 7).

The 1.67–1.70 Ca/P ratio found in powders after mechanochemistry was not incompatible with the appearance of β-TCP after powder heating in the presence of silica because the Ca/(P + Si) ratio was lower than 1.67. Wollastonite-2M (CaSiO3) has only one important diffraction peak, at 2θ = 29.96° (plane 3.2.0, JCPDS file #75-1396); its other peaks are of low intensity. It was not detected in the XRD patterns presented in Fig. 5. The absence may be due to too small an amount (the peak is lost in the background) or by the overlapping of its main peak with the β-TCP peak at 2θ = 29.62° (plane 3.0.0, JCPDS file #70-2065) or the α-TCP peak at 2θ = 29.70° (plane 5.1.0, intensity 20%, JCPDS file #9-348). Similarly, CaSiO3 was not detected by Langstaff et al. in their XRD patterns. However, CaSiO3, even in the amorphous state, is a basic compound [30] and its formation during heating in the presence of porcelain could explain the basicity of our powders after heating (positive pH test). Finally, during the powder dissolution in HCl for calcium and phosphate analyses, calcium was removed from CaSiO3 [30] (Eq. (8)) and the Ca/P ratio found, equal to the Ca/P ratio in the starting materials, was logical:

\[
\text{CaSiO}_3 + 2\text{HCl} \rightarrow \text{Ca}^{2+} + 2\text{Cl}^- + \text{SiO}_2 \downarrow + \text{H}_2\text{O} \tag{8}
\]

4.4. Origin of the powder pollution by mill material

In mechanochemistry with a ball milling device, the activation energy of the reaction was provided by shocks between the balls or the ball and vial walls. During the shocks, erosion of the ball or vial wall surfaces cannot be excluded due to the brittleness of the material. Thus, the powder contamination appeared as an inherent drawback of the technique, unless very special precautions are taken to avoid/minimize it (see Ref. [8], p. 136).

Results show clearly that the powder pollution by mill material was much lower for the dry than for the wet mechanochemistry, and that the specific hourly degree of pollution increased linearly with the percentage of water in the slurry (Fig. 7, Eq. (4)). Moreover, as the mechanochemical reaction rate is lowered by the addition of water, the total powder pollution during wet mechanochemistry is much greater than during dry grinding. A possible hypothesis is as follows (Fig. 9).

(1) During dry grinding: (i) Balls are covered by powder and the thickness of the powder layer increases with the amount of powder [39]; (ii) during a shock, powder is first compacted; (iii) air bubbles included between powder grains are adiabatically compressed (Fig. 9 top), provoking a local increase in temperature that, combined with the mechanical effect, activates the reaction rate; and (d) the balls being covered by powder, there is no or very few direct contacts between them and consequently low ball erosion, thus low pollution. This last point was reinforced by pollution measurements carried out by Mochales et al. [40], which showed that the degree of pollution decreases linearly with the mass of powder ground for the same total mass and surface area of balls and a given material.

![Fig. 9. (Top) Schematic representation of a ball impact during dry mechanochemistry. The powder is compacted with the adiabatic compression of air bubbles, which increases the reaction rate and creates a protective powder layer against ball erosion, minimizing powder pollution. (Bottom) Schematic representation of a ball impact during wet mechanochemistry; suspension is ejected from the impact zone, decreasing the reaction rate and increasing the direct contact between balls, thus increasing powder pollution.](image-url)
(2) During wet attrition: (i) The more fluid the slurry, the less covered by powder in suspension are the balls; (ii) water being incompressible, during a shock, the suspension will be partly ejected from the impact zone (Fig. 9 bottom) without any significant temperature increase; and (c) because the suspension fluidity increases with the water percentage, the higher the water percentage, the lower the thickness of the suspension layer entrapped between the balls or between the ball and vial wall during an impact. This has two consequences: First, the amount of powder crushed (thus that can react) at each impact being decreased, the reaction rate will be lowered; and, secondly, direct contacts between balls or ball and vial wall will be more numerous (no protective powder layer), leading to a greater erosion of balls and thus much more powder pollution.

The potential or real powder pollution by mill material was rarely mentioned in papers concerning wet or dry mechanochemistry of calcium phosphates. Starting from DCPD and CaCO₃ with an initial Ca/P ratio of 1.67, a water percentage of 87% in the slurry and using first a Teflon jar and zirconia balls, Toriyama et al. [11] obtained a final powder composition of HA 80% + β-TCP 20% after firing at 1250 °C. In another experiment, alumina and silica (2 and 6 wt.%) were intentionally added to the starting materials and the final composition after heating was HA 13% + β-TCP 87%. In a third experiment the Teflon jar was replaced by a porcelain jar and the final composition was HA 34% + β-TCP 66%, but with a 40 wt.% contamination by mill material (ZrO₂ 15%, SiO₂ 15%, Al₂O₃ 9% and K₂O 1 wt.%). The observed high level of contamination corresponded to the pollution we measured with the same water percentage in the slurry and, very likely, the high β-TCP percentage obtained in Toriyama’s last two experiments was due to the presence of silica intentionally added or coming from porcelain.

Suchanek et al. [14,16,18] wet mechano-synthesized HA using a different milling device (multi-ring media mill with ZrO₂ milling rings), a completely water-soluble phosphate source ((NH₄)₂HPO₄) and a poorly water-soluble calcium source (Ca(OH)₂ or CaCO₃) with an initial Ca/P ratio of 1.67, a water percentage of 87% in the slurry. They obtained pure HA without β-TCP after heating at 900 °C and a very small amount after heating at 1100 °C. They did not report any powder contamination by zirconia. Perhaps this point was not investigated, or the level of pollution was low and not visible on XRD patterns, because grinding was produced by friction between disks or disks and vial wall instead of impacts between balls in planetary ball mill, which would consequently be more polluting than the multi-ring media mill. ZrO₂, if present, would not have had the same influence as SiO₂ on HA decomposition. These points still need to be investigated for future developments of either dry mechanochemical or mechanochemical–hydrothermal synthesis of calcium phosphates.

A simple test to verify the eventual contamination of mechano-synthesized powder by mill material is the accurate weighing of balls before and after grinding. This test is easily feasible for the ball mill, but not for the multi-ring media mill. We are currently using this test to investigate the powder contamination by different mill materials and experimental conditions, and the results will be published soon. Note that each grinding step in a process, for example to reduce the particle size, is potentially polluting.

5. Conclusion

From this work, one can conclude that, when using a planetary ball mill, dry mechanochemistry is preferable to wet mechanochemistry for two main reasons: (i) Reactions are faster without the addition of water; and (ii) a very low level of pollution by the mill material is observed (<0.3 wt.% after a 10 h grinding time). Consequently, the final phases are not affected by mill material and the final products have the expected Ca/P ratio. Finally, powder obtained by dry mechanochemistry can be used directly, without filtering and drying stages, to prepare bioceramics [41].

References


