# Calcium apatite prepared from calcium hydroxide and orthophosphoric acid

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Calcium hydroxyapatite has been prepared due to a direct precipitation reaction between 0.3 M orthophosphoric acid solution and 0.1 mol calcium hydroxide dispersed in 200 ml water. The effect of the addition rate of the acid solution, reaction temperature and mixing molar Ca/P ratio is examined on the thermal stability and stoichiometry of the precipitates. Optimum conditions for HAp suitable for dense ceramics are derived from the results. The non-stoichiometry is interpreted in terms of the pH profile in the vicinity of the hydroxide particles and the state of the orthophosphate ions.

1. Introduction

Hydroxyapatite $(Ca_5(PO_4)_3OH$ or $Ca(OH)_2 \cdot 3Ca_3(PO_4)_3$, HAp) is a primary constituent of human hard tissues like bones and teeth. HAp ceramics have a potential for application to artificial tooth roots or filler for bone defects since new bone tissues grow on the implanted HAp ceramics to be tightly bonded. Several methods have been proposed for HAp from aqueous solution [1]. Asada *et al.* [2] previously prepared HAp powders under ammonia-alkaline conditions.

$$5Ca(NO_3)_2 + 3NH_4H_2PO_4 + 7NH_4OH$$
$$\longrightarrow Ca_5(PO_4)_3OH + 10NH_4NO_3 + 6H_2O$$
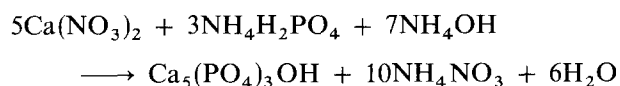
The reaction conditions were easily controllable to prepare HAp of good sinterability. It was disadvantageous however in that not only excess amount of ammonia was necessary but also washing and rinsing with a greater amount of water were inevitable in order to eliminate ammonium nitrate and residual ammonia.

Akao *et al.* [3] prepared HAp from a reaction

$$5Ca(OH)_2 + 3H_3PO_4$$
$$\longrightarrow Ca_5(PO_4)_3OH + 9H_2O$$
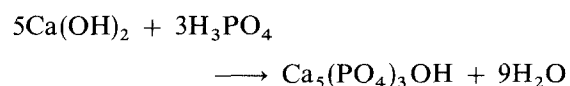
They studied mechanical properties of the HAp ceramics but did not clarify the correlation between precipitation conditions and properties of the powder. Since calcium hydroxide is less soluble in water and the state of the orthophosphate ions depends on pH, the precipitation reaction involves the dissolution of calcium hydroxide, diffusion of the ionic species such as Ca^{2+} and hydroxide ions, and electrolysis of the orthophosphate ions. These bring complexity in controlling the reaction conditions for the powder of desired characteristics. However, this method is pre-sumably suitable for an industrial production of HAp since only the by-product is water.

In the present study we have examined the effect of the reaction temperature, rate of mixing solutions, and mixing molar ratio Ca/P on the properties of the HAp powders. The stoichiometry of the precipitate is discussed on the basis of the experimental results and it is correlated with the pH of the system and the state of the orthophosphate ions. The optimum conditions are derived for preparing thermally stable HAp powders suitable for HAp ceramics.

2. Experimental details

2.1. Preparation

Reagent grade 0.10 mol calcium hydroxide were dispersed in well degassed 200 ml distilled water. Under rigorous stirring 0.3 M orthophosphoric acid solution was added at various rates in drops to the suspension at 0 to 100 °C until the mixing molar ratio Ca/P reached the predetermined value. In the course of addition the pH was monitored with a calomel electrode and a pH meter. After completion of the addition the HAp suspension was subjected to the ripening (ageing) treatment: the suspension was refluxed for 20 min followed by stirring for another 25 min without heating before it was left unstirred for over 10 h. The HAp precipitates were separated from the suspension with a vacuum filtration technique. The filtered cake was placed in an oven kept at 40 °C, and the temperature was raised gradually up to 80 °C over 24 h and was maintained there for 5 to 7 h.

2.2. Crystallite size

The X-ray diffraction (XRD) technique was used not only to identify the phases in the as-dried or heated

precipitates but to evaluate the average particle size D by the use of Sherrer formula [4].

$$D = 0.9\lambda/B\cos\theta \qquad (1)$$

Here λ is the wavelength of the X-ray (0.1542 nm (CuK_α) for the present experiment), θ is the diffraction angle, and B (in radian) the measured width at half height of the diffraction peak. We used (0 0 2) diffraction of HAp with $2\theta = 25.8°$ after JCPDS 9-432. The specific surface area (SSA) was measured for the dried samples due to the nitrogen BET method. With the SSA values an average particle size D of the precipitate were also evaluated with Equation 2 assuming that the crystallites were cubic.

$$D = 6/(d\,S) \qquad (2)$$

where d and S were the density and SSA value, respectively.

2.3. Thermal shrinkage and surface morphology of HAp ceramics

A rod of 5 mm in diameter and 10–11 mm in length was cut out from the dried cake, for which the thermal expansion/shrinkage was measured with a heating rate of $10°C\,min^{-1}$. The fractured surface of sintered bodies was etched with 0.1 M lactic acid for 1 min and was observed under an SEM (JEOL JSM-T20) with 20 kV acceleration.

3. Results and discussion
3.1. Thermal stability of the HAp precipitates
3.1.1. The rate of addition of the orthophosphoric acid solution
In order to attain the Ca/P mixing ratio = 1.67, 200 ml 0.3 M phosphoric acid solution were added in drops to the freshly prepared suspension of 0.1 mol calcium hydroxide at 25 °C at the rate of 5 to $33\,ml\,min^{-1}$. The suspension remained alkaline (pH > 8) and the precipitates for any additional rate gave only an XRD pattern of HAp, a typical example of which was shown in Fig. 1a for the additional rate of $33\,ml\,min^{-1}$. When the phosphoric acid solution was added at a time, the pH was near 5 at first and then reached 7 at the completion of the reaction in 3 min. In this case an unknown phase was seen in the XRD pattern (Fig. 1b). The heat treatment of this precipitate at 1250 °C for 3 h yielded HAp and α-tricalcium orthophosphate $(Ca_3(PO_4)_2, TCP, JCPDS$ 9-348), as shown in Fig. 1c. It is indicated that the unknown phase is a precursor of TCP and that too high an addition rate of the phosphoric acid solution introduces a Ca-deficient precipitate. In order to prepare stoichiometric HAp, therefore, the suspension should remain well alkaline with a controlled rate of addition of the phosphoric acid solution.

3.1.2. The ripening treatment
The HAp precipitates were prepared at 25 °C by adding so much orthophosphoric acid solution at the rate of 10 ml min^{-1} as to attain the mixing molar ratio Ca/P = 1.68, slightly richer in Ca than the stoichi-
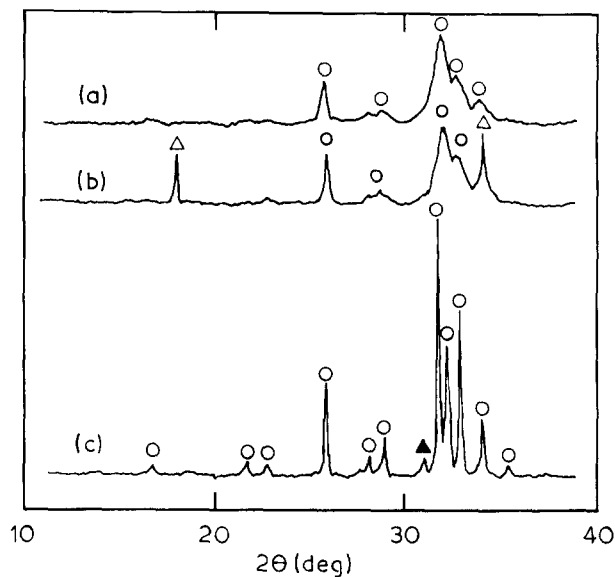

Figure 1 X-ray diffraction patterns of HAp precipitated at 25 °C for mixing ratio Ca/P = 1.67. The H_3PO_4 solution was added, (a) at the rate of 33 ml min^{-1}, (b) at a time; (c) the pattern of sample (b) after the treatment at 1250 °C for 3 h, ($\bigcirc$) HAp, ($\triangle$) Unknown, ($\blacktriangle$) α-TCP.

ometry. The XRD patterns indicated that the ripening improved crystallinity of the particles. Thermogravimetric (TG) analysis up to 1200 °C showed a greater weight loss (17 wt %) for the sample without ripening than that for the ripened sample (10 wt %). β-TCP was formed in the samples without ripening due to the heating below 900 °C, while HAp in the ripened samples was stable up to 1300 °C where it decomposed to α-TCP. These experimental results suggest the powder without the ripening treatment include non-stoichiometric apatites which are deficient in Ca or contain water [5, 6]. The ripening treatment is therefore necessary in order to prepare thermally stable HAp.

3.1.3. Reaction temperature
From the stoichiometric mixing Ca/P ratio HAp was precipitated at various temperature. The rate of addition of the phosphoric acid solution was 10 ml min^{-1}. β-TCP appeared in the precipitates prepared at or below 60 °C due to the heat treatment at 1200 °C for 3 h. Fig. 2a–d are scanning electron microscopy (SEM) photographs of the fractured surfaces of HAp ceramics sintered at 1200 °C for 3 h by the use of the powder precipitated at different temperatures. The grain size was almost independent of the reaction temperature but the ceramics from the higher temperature ($\geq$ 40 °C) powder had a number of voids. This can be attributed to morphology of secondary particles in the as-dried powder. The higher reaction temperature gives well grown primary crystallites, as shown below, and thus less dense secondary aggregated particles. The green compacts from them accordingly involves a large fraction of void space. In the course of sintering such spaces may gather up to be the voids shown in Fig. 2, preventing densification. Indeed, though not illustrated here, the thermal shrinkage of the green compacts from the low temperature
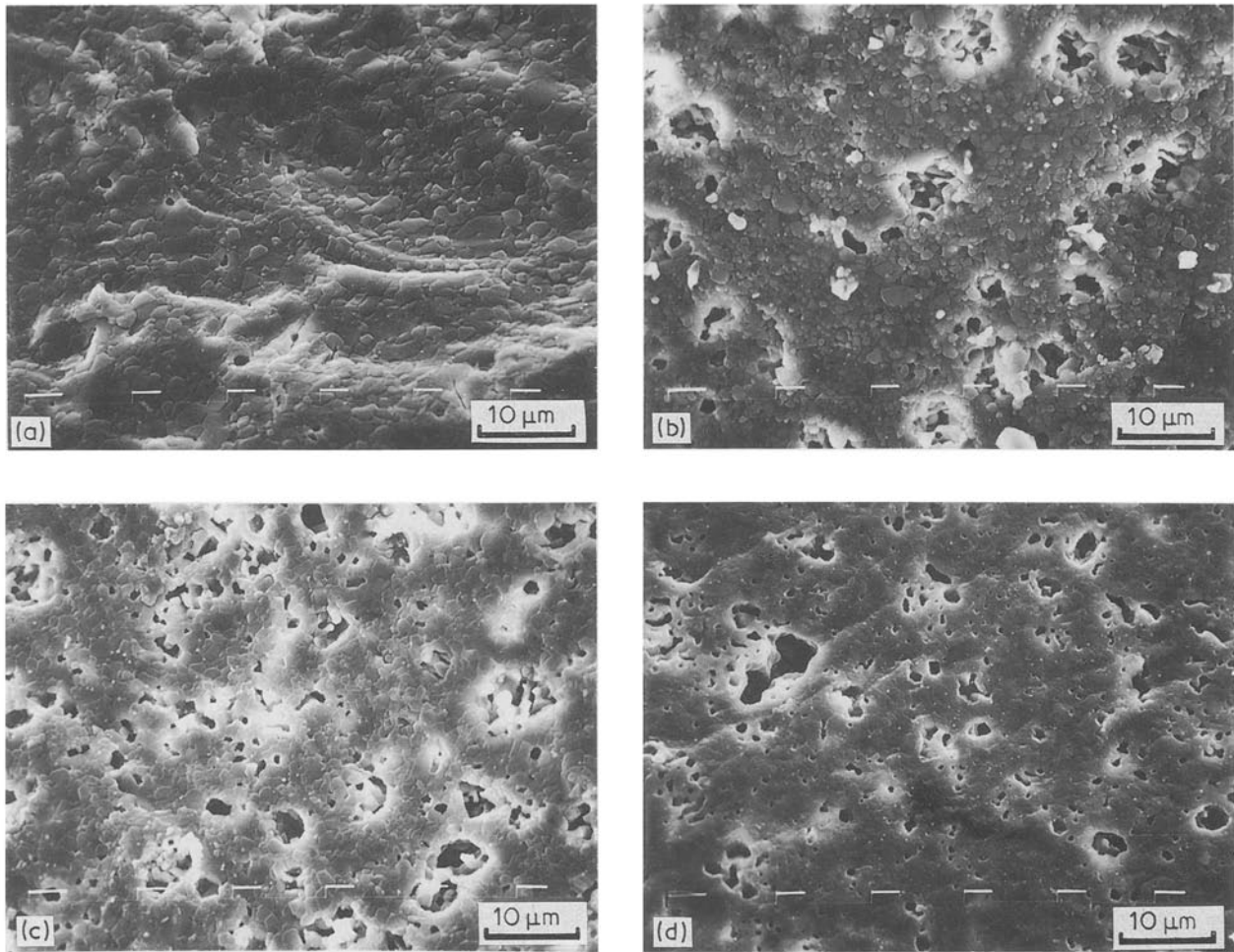
Figure 2 The fractured surface of ceramics due to sintering the HAp powders for Ca/P = 1.67 at 1200 °C for 3 h (etched with 0.1 M lactic acid for 1 min). HAp powders were precipitated at, (a) 10, (b) 40, (c) 60 and (d) 80 °C.

powders became significant at lower sintering temperature (the better sinterability), resulting in denser ceramics than those from the high temperature powders. The lower thermal stability of the low temperature powder can be overcome by the use of much slower addition of the phosphoric acid solution and proper ripening treatment since it is caused by the Ca-deficiency, as is suggested from the results described above.

3.1.4. The mixing Ca/P ratio

The orthophosphoric acid solution was added to the calcium hydroxide suspension at 25 °C so as to vary the Ca/P ratio from 1.29 to 1.99. The as-dried precipitates all showed the XRD pattern of HAp, while their thermal decomposition behaviour depended on the Ca/P ratio. Fig. 3 is a pseudo-phase diagram of the present system, illustrating the crystal phases in the precipitates after the heat treatment as a function of the mixing Ca/P ratio. TCP appeared at higher temperatures with an increase in the Ca/P ratio. Calcium oxide was found for Ca/P > 1.7. The most thermally stable HAp was prepared with nearly stoichiometric mixing ratios from 1.68 to 1.70.

3.2. Crystallite size and shape

The crystallite size of the precipitates from the stoichiometric mixture was plotted in Fig. 4 as a function

of the reaction temperature. Each crystallite size from Equations 1 and 2 agreed well with the other and increased with the reaction temperature. Fig. 5 shows the effect of the mixing Ca/P ratio on the crystallite size for the 25 °C precipitates. The size from the XRD due to Equation 1 remained almost constant while
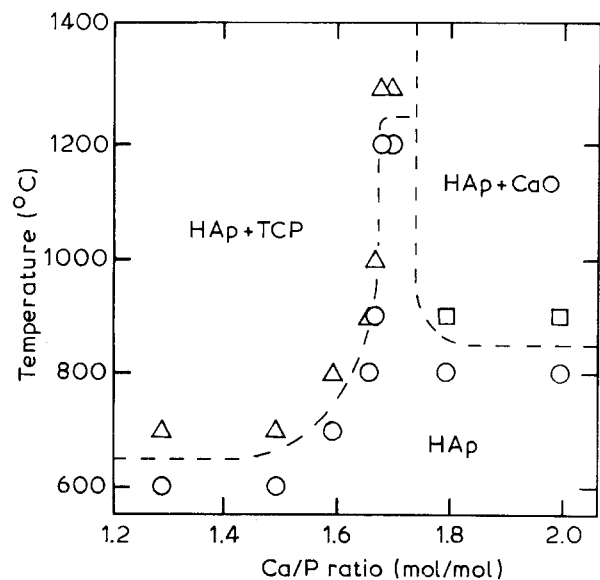

Figure 3 A pseudo-phase diagram, showing thermal stability of HAp prepared at 25 °C as a function of the mixing molar ratio Ca/P.
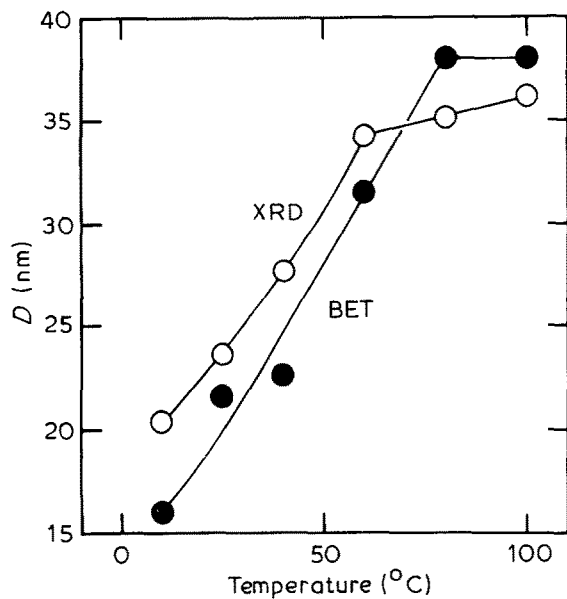
53

Figure 4 Crystallite size D of HAp for the mixing ratio Ca/P = 1.67, derived from Equations 1 (XRD) and 2 (BET), plotted against the precipitation temperature.

that from SSA due to Equation 2 decreased. A simple calculation derives Equation 3 for an averaged crystallite size from a value of SSA where hexagonal crystallites of an aspect ratio $k = a/c$ are assumed to be of cubic symmetry.

$$D_{cubic} = 3c(1 - 2/[(3)^{1/2}k + 2])$$ (3)

A plate-like crystal has a larger value of $k(>1)$ and a needle-like crystal has a smaller value of $k(<1)$. A larger average crystallite size will be obtained from Equation (3) for a larger aspect ratio k, and vice versa. Fig. 5, consequently, indicates that the HAp crystallites become more needle-like with the increase in the mixing Ca/P ratio.
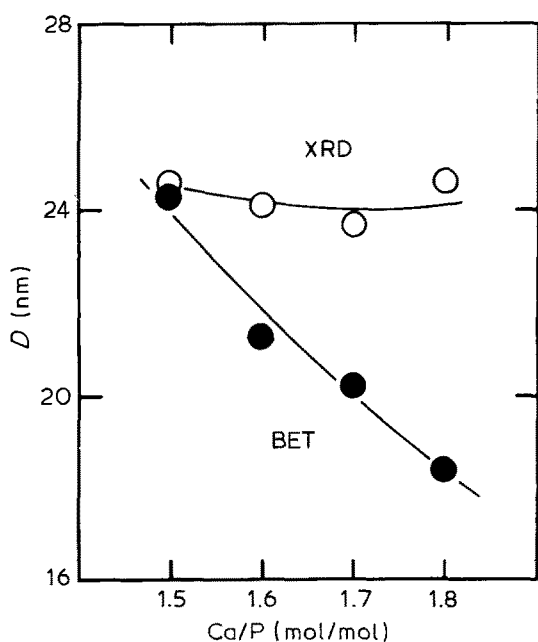

Figure 5 Crystallite size D of HAp precipitated at 25 °C, derived from Equations 1 (XRD) and 2 (BET), plotted as a function of the mixing molar ratio Ca/P.

3.3. The stoichiometry of the HAp precipitates
3.3.1. Presence of carbonate apatite

Fig. 6 illustrates infrared (IR) spectra of the powders from various mixing Ca/P ratios after the heat treatment at temperatures indicated. All samples had a similar IR profile. The PO_4 bands were near 600 and 1100 cm^{-1} (very strong) as well as at 470 cm^{-1} (weak but sharp). No sharp peak appeared in the spectra for as-dried or heated samples around 753 cm^{-1} assigned by Monma and Kanazawa [7] to the pyrophosphate ion $P_2O_7^{4-}$. Adsorbed or structural [6] water molecules gave a band near 3400 cm^{-1}. A sharp 3580 cm^{-1} band was due to the structural hydroxyl ions. The O–H band for a P–OH bond [7, 8] was at 877–900 cm^{-1}, as found for alkaline earth monohydrogen orthophosphates [9], and was much stronger in the as-dried powders as in the hydrated TCP [7].

The spectra for Ca/P > 1.67 had a broad band at about 1450 cm^{-1} assigned to carbonate ions, a trace of which was also seen in the spectra for the Ca/P < 1.67 samples. The carbonate ions possibly came into
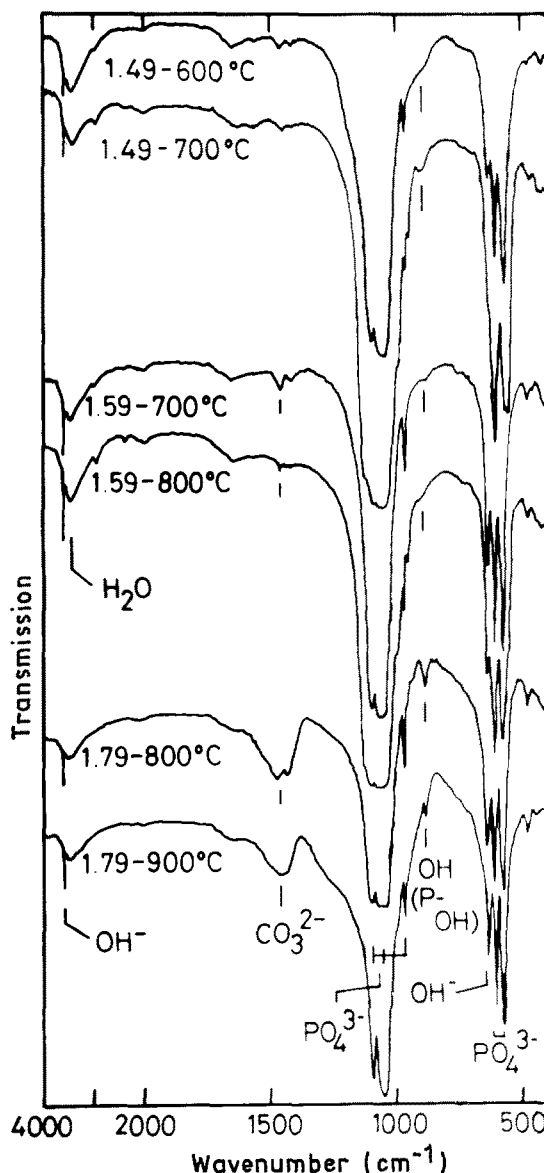

Figure 6 Infrared spectra of HAp for a few mixing Ca/P ratios after the heat treatment at the temperature indicated.

54

the system from the air at the precipitation process because the reaction system was open to air in the present experiment. At an early stage of the phosphoric acid addition the suspension was highly alkaline regardless of the mixing Ca/P ratio and readily absorbed CO_2 in the air but this was not the case for the smaller Ca/P ratios at the end of the addition where the suspension was less alkaline. It is reasonable therefore that Fig. 6 indicates the much stronger carbonate band for larger Ca/P ratios than for the smaller ones. Since XRD could not confirm the presence of calcium carbonate in any samples the carbonate ions were presumably involved in the crystal structure, that is, a carbonate apatite was also precipitated.

3.3.2. The phosphate equilibrium and non-stoichiometry

On the basis of the results described above in Section 3.1, it is obvious that Ca-deficient HAp is very easily prepared due to improper precipitation conditions. This is not surprising because a wide range of non-stoichiometry is allowed in the apatite systems [10]. A few theories have been proposed to explain the non-stoichiometry of HAp, and been summarized by Bett et al. [8]. From the experimental results described above, the Ca-deficiency in the present HAp can be attributed to too high addition rates of the orthophosphoric acid or low mixing Ca/P ratios and can most likely be interpreted in terms of the presence of the monohydrogen orthophosphate anion, HPO_4^{2-} [7, 8]. The hydroxyl ions originally present in the calcium hydroxide suspension are readily exhausted by the phosphoric acid under a very high addition rate, lowering pH in the bulk apart from the calcium hydroxide particles far below 12.3, pK_a of the reaction [11].
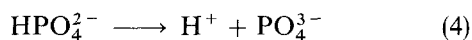
$$HPO_4^{2-} \longrightarrow H^+ + PO_4^{3-} \quad (4)$$

Fig. 7 schematically illustrate the variation in pH as well as the concentration profile of the calcium and orthophosphate ions in the solution. The locations for the equilibrium between the phosphate anions depends on the precipitation conditions. Near the vicinity of the particle surface the pH is maintained high enough to yield HAp of near stoichiometric composition even in the low Ca/P suspension as far as the particles remain. In the bulk, however, pH lower than about 12 favours the precipitation of an apatite including HPO_4^{2-}. At slower addition of the phosphoric acid the HPO_4^{2-} ions sitting at a growing cite will meanwhile be brought into contact with the hydroxyl ions and changed to PO_4^{3-} ions according to Equation 4. Therefore, the Ca-deficiency due to the low temperature preparation can be explained as: the rate of dissolution of calcium hydroxide may be depressed with a decrease in temperature and the phosphoric acid solution was added under too high a rate to keep the suspension very alkaline during the reaction. Once, however, non-stoichiometric crystals grow, it may take a longer time for ripening than applied in the present experiment in order to establish the stoichiometry.

4. Summary

Calcium hydroxyapatite (HAp) has been prepared due to the precipitation reaction with addition of orthophosphoric acid to calcium hydroxide suspension. The very high addition rate, low mixing Ca/P ratio yielded Ca-deficient HAp of lower thermal stability. The lower reaction temperature gave smaller particles with slight non-stoichiometry. On the basis of the experimental results it can be concluded that the stoichiometric HAp precipitate of very fine particles suitable for dense ceramics is obtained by slower addition of the phosphoric acid at lower temperature followed by the appropriate ripening procedure. The non-stoichiometric HAp otherwise is readily precipitated because the pH is lowered in the vicinity of hydroxide particles where HPO_4^{2-} ions are stable instead of PO_4^{3-} ions.

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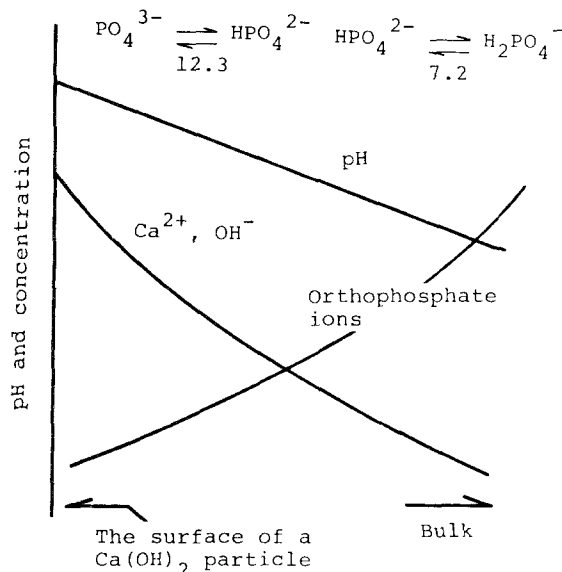
Figure 7 A schematic representation of the pH profile and concentration profiles of the ionic species. The lines only show variation trends and have no theoretical significance. Pairs of orthophosphate ions in equilibrium are indicated together with pK_a values.