AQUEOUS COLLOIDAL PROCESSING OF FLUORAPATITE BODIES

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ABSTRACT

In order to produce stable aqueous fluorapatite (FA) suspensions, its surface reactivity in an aqueous solution having two initial pH values with a concentration of ammonium polyacrylate (NH₄PA) was investigated as a function of time. The influence of the slip viscosity on the casting rate and the microstructure of the resultant green slip cast compacts was determined. Upon the FA introduction in the aqueous solutions, an initial release of F anions located at the surface was found, which was not dependent of the pH and the presence of dispersant. The increase in the initial pH of the solution above 7 and/or the addition of NH₄PA markedly reduced the Ca⁺⁺/ H⁺ exchange reaction rate. As a result, well-stabilized concentrated aqueous suspensions could be obtained at pH close to 9. The greater permeability of cakes produced from slips with high viscosity values (0.5 wt% PVA) increased the casting rate.

Keywords: fluorapatite, surface reactivity, casting rate.

1. INTRODUCTION

Calcium orthophosphates such as fluorapatite $(Ca_{10}(PO_4)_6F_2)$ are widely used as bone substitute materials due to their chemical similarity to the mineral component of mammalian bones and theeth (1). Fluorapatite is non-toxic, biocompatible, not recognized as foreign material in the body and, most importantly, exhibits bioactive behaviour and integrates into living tissue by the same processes active in remodelling healthy bone. These charasteristics lead to an intimate physicochemical bond between the implants and bone, termed osteointegration (2). Even so, the major limitations to use fluorapatite as load-bearing biomaterials is its mechanical properties, it is brittle with a poor fatigue resistance (3). That is why, in biomedical applications fluorapatite is used primarily as fillers and coatings. Bioinert ceramic such as porous ZrO_2 can be coated with FA to achieve a high mechanical strength as well as a suitable biocompatibility of the system (4). A relatively thick FA coating layer on ZrO_2 can be fabricated by dip coating.

The first step in this process, is the preparation of stable concentrated FA suspensions with the addition of a dispersant and a binder. Anionic polyelectrolytes such as NH₄PA are commonly used as dispersant of ceramic powders in aqueous media (5). The polyelectrolyte adsorbs at the solid-liquid interface and infers repulsive force between the particles which keeps the particles well dispersed; the repulsive interactions are caused by electrostatic and steric effects (6). The binder provides strong adhesion between the ceramic particles and the substrate, preventing the powder from detaching off the substrate during thermal treatment. PVA is frequently used in an aqueous media due to its affinity with the processing liquid.

The preparation of stable suspensions in aqueous solution is strongly limited by the solubility of FA, which is rather high in acidic conditions. Little attention has been paid to the study of its surface reactivity in an aqueous solution with NH₄PA in weakly alkaline conditions, at which the anionic polyelectrolyte is dissociated. In order to produce well-stabilized slips, first its surface reactivity in an aqueous solution having two initial pH values with a concentration of NH₄PA, was investigated as a function of time.

The layer formation process by dip coating is similar to the formation of a cake on a porous mold by slip casting (7), in both the driving force for the liquid flow is the capillary suction pressure of the substrate. The rheological behaviour of the suspensions greatly affects the growth rate of the cake and the resultant green density. Therefore, the casting rate of well stabilized 38 vol.% FA slips with and without PVA, and the resultant green body microstructure were examined and related to the degree of slip dispersion.

2. EXPERIMENTAL PROCEDURE 2.1. Materials

The $Ca_3(PO_4)_2$ (Fluka, Germany) and CaF_2 (Sigma–Aldrich, Ireland) powders were mixed in a 3:1.5 ratio; thus, CaF_2 was in excess with respect to the stoichiometric ratio for the reaction:

$$3 \operatorname{Ca}_{3}(\operatorname{PO}_{4})_{2} + \operatorname{CaF}_{2} \rightarrow \operatorname{Ca}_{10}(\operatorname{PO}_{4})_{6}\operatorname{F}_{2}$$
(A)

The mixture of powders was calcined 3 hs at 1000 °C. Then, the powder was milled in an attrition mill using 1.6 mm zirconia balls with 0.047 wt% NH₄PA during 48 hours. The powder was added in portions to the suspension and the pH was manually adjusted to be maintained at 9 during the additions. The milled powder was washed with distilled water and dried at 100 °C. This powder subsequently referred as FA was used for the experiments presented in this study.

A commercial ammonium polyacrylate solution (Duramax D 3500, Rohm & Haas, Philadelphia PA) and a 9 wt% PVA solution were used as deflocculant and binder, respectively.

2.2 Powder characterization

The chemical composition of the powders was determined after alkaline fusion. The crystalline phases in the FA powder were determined by X-ray diffraction (XRD) using a diffractometer Philips PW3710

In order to estimate the isoelectric point (IEP) of the FA, mean particle diameter measurements of 1.1 vol.% suspensions with 0 and 0.56 wt% NH_4PA at different pH values were developed using a Sedigraph (Micromeritics, USA).

2.3 FA surface reactivity measurements

Three suspensions having a FA content of 10.4 vol.% were prepared as follows: (1) FA was added to distilled water , (2) FA was added to distilled water with 0.6 wt% NH₄PA at an initial pH 7.7, and (3) FA was added to an aqueous solution having an initial pH of 8.9 with 0.6 wt% NH₄PA. The aqueous dissolution behaviour of FA was study by measuring the pH of the suspensions and the Ca/P, F/P atomic ratio in the solid phase, as a function of time for the 1, 2 and 3 slips. The Ca/P and F/P atomic ratios were determined by chemical analysis and energy-dispersive x-ray analysis (SEM-EDX, Philips 505 equipment with EDX accesory) after centrifugalize

the suspensions, washing the powders twice with distilled water and drying them at 100 °C.

2.4 Slip casting and characterization of green samples

38 vol% suspensions with 0.6 wt% NH₄PA and two PVA concentrations: 0 and 0.5 wt% were used to study the slip casting process. We have previously measured the relative viscosity $\eta_{r=} \eta_s/\eta_f$, where η_s and η_f are the viscosities of the suspension and the fluid medium (PVA + water+ dispersant), respectively, for 38 vol.% FA slips with 0.6 wt% NH₄PA without PVA and with 0.5 wt% PVA (8). The relative viscosity values (at a shear rate of 126 s⁻¹) were 11.8 and 58.8 for the slips with 0 and 0.5 wt% PVA, respectively.

The slip casting process could be described as one-dimensional filtration, the slips flow unidirectionally through a cylindrical plaster mold. The casting rate of stabilized 38 vol.% slips with 0 and 0.5 wt% PVA was determined by measuring the thickness of the cake as a function of time. The thickness was measured for times \geq 60 min, since for shorter times the error was high. The consolidated disks of diameter 2 cm were dried at room temperature and then at 100 °C.

The density of green compacts was determined by the Archimedes method using mercury displacement. The pore size distribution of green cakes was measured by mercury porosimetry (Porosimeter 2000 Carlo Erba, Italy).

2.5 Sintering and characterization of sintered samples

Green cylinders were sintered at 1200 °C, using a heating rate of 5 °C/min. The bulk density of the samples was measured by water inmersion (Standard Method ASTM C20).

3. RESULTS AND DISCUSSION

3.1. Powder characterization

The chemical composition of the calcined powder indicated an excess of Ca and F with respect to the theoretical composition of $Ca_{10}(PO_4)_6F_2$. This was attributed to the excess of CaF_2 used in the preparation of fluorapatite (eq. A). Ca and F were removed during the milling and washing of the calcined powder, leading to an apatite

with a Ca/P atomic ratio and a F content of 1.67 and 37700 ppm, respectively, which were close to the theoretical one. The average composition of the FA powder was found to be $Ca_{10}(PO_4)_6F_2$; the XRD patterns of FA corresponded to JCPDS # 15-0876; no additional phases were revealed.

Figure 1 shows the mean particle diameter (d_{50}) as a function of pH for FA with 0 and 0.56 wt% NH₄PA. The FA could be dispersed at pH values >6; the d_{50} slightly decreased with increasing pH from 6.5 to 9.9, reaching at this pH the lowest mean particle diameter of 0.75 µm. An important increase in the mean particle diameter was found with decreasing pH from 6 to 4; at pH ≤4 the d_{50} remained nearly constant.



Fig.1: Mean particle diameter (d_{50}) as a function of pH for FA with different NH₄PA contents: (a) 0 wt%, (b) 0.56 wt%.

The degree of aggregation of FA in aqueous dispersion was determined by the magnitude of the powder surface charge. At pH <6.5 a reduction in the electrostatic repulsion between particles was expected due to the strong flocculation; the Van der Waals attraction forces were dominant and caused aggregation of the particles. In the pH range from 6.5 to 10 the particles became well dispersed indicating an increase in the electrostatic repulsion between particles. At pH ≤4 an increase in the repulsion between particles could be expected due to the high positive charge of the FA powder; however, the aggregation between particles still remained. This behaviour could be attributed to proton exchange reactions at the FA surface under

strongly acidic conditions, which will be explained later. The IEP of FA seemed to be about pH 6. Fluorapatite surfaces are thought to consist of two distinct surface groups \equiv CaOH₂⁺ and \equiv PO⁻ [9]. The \equiv CaOH₂⁺ concentration decreases with increasing pH and at pH>9.5 the \equiv PO⁻ sites predominate (9).

The addition of NH₄PA shifted the curve towards lower pH values (Fig. 1). A well dispersed FA suspension was found at pH \geq 5, the mean particle diameter was nearly the same as the FA powder. At pH values lower than 4.5 flocculation occurred; however, aggregation of particles was lower than that observed in the absence of the dispersant. The ammonium polyacrylate dissociation according to the reaction:

 $\mathsf{RCOONH}_4 \to \mathsf{RCOO}^- + \mathsf{NH}_4^+ \tag{B}$

begins at pH>3.5; at pH values \geq 8.5 the polymer charge is negative with the degree of ionization approaching 1(6). The RCOO⁻ groups of the deflocculant were adsorbed at the positive \equiv CaOH₂⁺ sites of the FA powder surface. The anionic polyelectrolyte was only slightly dissociated at pH <8.5; consequently, the electrostatic repulsion between the polyelectrolyte chains were of less importance and the steric contribution started to dominate.

3.2. FA surface reactivity

Figures 2 and 3 show the pH of the suspensions and the Ca/P, F/P atomic ratios in the solid phase, respectively, as a function of time for the 1, 2 and 3 slips.



Fig.2: pH as a function of time for three 10.4 vol% FA suspensions: (1) FA added to distilled water, (2) FA added to distilled water with 0.6 wt% NH₄PA at an initial pH 7.7,

and (3) FA added to an aqueous solution having an initial pH of 8.9 with 0.6 wt% NH₄PA.

The Ca/P and F/P atomic ratios during the dissolution differed from those of the dissolving stoichiometric apatite (Ca/P=1.67 and F/P=0.33), suggesting that the release of Ca and F were non-stoichiometric with respect to phosphorous for the three suspensions. For the 1 slip, an important adsorption of OH⁻ was found upon the FA introduction in aqueous solution, since at pH 7, which was close to the IEP of the FA powder, a high amount of positive surface groups still remained. As a result, the pH decreased to an acidic value up to a minimum of 4.8; along with OH⁻ adsorption a rapid removal of F from the near surface was found. Afterwards, the F/P atomic ratio remained nearly constant with increasing time up to 7 days, while the Ca/P atomic ratio decreased and the pH increased. Thus, after the initial preferential release of F relative to P, an exchange reaction between H⁺ and Ca⁺⁺ was involved in the uptake of H⁺ by FA surfaces, in accord with:

 $Ca_{10}(PO_4)_6F_2 + 2x H^+ \leftrightarrow [Ca_{10-x}(HPO_4)_{2x}(PO_4)_{6-2x}]^{+2} + x Ca^{++} + 2F^-$ (C)

Fig.3: Ca/P and F/P atomic ratios in the solid phase as a function of time for three 10.4 vol% FA suspensions: (1) FA added to distilled water , (2) FA added to distilled water with 0.6 wt% NH_4PA at an initial pH 7.7, and (3) FA added to an aqueous solution having an initial pH of 8.9 with 0.6 wt% NH_4PA .

10

Time (days)

14

16

18

12

Chaïrat et al.(9) found that the Ca removal was coupled to phosphate hydrolysis and leaded to the formation of a protonated Ca-leached layer at FA surface. Thus, after the initial stage, proton consumption and release of Ca by Ca⁺⁺/ H⁺ exchange

reaction occurred with increasing pH of the solution and decreasing the Ca concentration in the solid phase accordingly. The same slope of the pH curve from 7 to 17 days indicated that the Ca⁺⁺/ H⁺ exchange reaction rate did not change (Fig.2). However, the slope of the Ca/P curve decreased and that of the F/P curve slightly increased (Fig.3). This was attributed to the detachment of phosphate anion together with Ca from the FA surface.

According to the results, a possible FA dissolution mechanism could consist in the following steps: (1) adsorption of OH⁻ at the positive surface groups and removal of F, (2) depletion of Ca and subsequent incorporation of protons, leading to the formation of a protonated Ca-leached layer; (3) detachment of phosphate tetrahedral together with Ca. This mechanism was in good agreement with that proposed by Dorozhkin (10) for the dissolution of apatite in acidic conditions.

The addition of FA to an aqueous solution with NH₄PA at pH 7.7 (2 slip), produced a lesser decrease in pH than that found for 1 slip. A minimum pH of 6.2 occurred at about 1 day (Fig. 2). The lower adsorption of OH⁻ was due to: (1) the FA powder had few positive surface groups at pH 7.7 since this pH was far from the IEP of the FA with NH₄PA (Fig. 1) and (2) the anionic polyelectrolyte slightly dissociated was adsorbed at some of the positive sites on the FA powder surface, leaving less ones for the OH⁻ adsorption. The lower slopes of the pH and Ca/P curves with respect to those for 1 slip, were attributed to the decreasing FA dissolution rate with increasing pH (eq. C).

The introduction of FA in an aqueous solution with the pH adjusted at 8.9 with NH₄PA produced a scarcely lower decrease in pH than that observed for the 2 slip (Fig. 2). The RCOO⁻ groups of the polyelectrolyte fully dissociated were adsorbed at some of the positive FA surface groups. However, as the amount of positive sites on the FA surface decreased with increasing pH, the powder had less positive groups at which the OH⁻ could be adsorbed. A minimum pH of 7.6 was found at about 1 day; for longer time the slopes of the pH and Ca/P curves were lower than those observed for the 1 and 2 slips (Figs. 2 and 3), due to the decreasing in the Ca⁺⁺/ H⁺ exchange reaction rate with increasing pH. The F/P curve was similar to that of the 1 and 2 slips up to 7 days, for longer time the slope was scarcely lower than those of the 1 and 2 slips. The dissolved P in the final stage of the dissolution (after 7 days) decreased with increasing pH as a consequence of the lesser protons penetration into the surface.

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The addition of FA to an aqueous solution with NH₄PA in weakly alkaline conditions (pH~9) produced the lowest decrease in pH, consequently the Ca removal and the up take of H^+ via proton–Ca exchange reaction were minimized.

During the aqueous colloidal processing of the FA powder the pH of the suspension was adjusted at 8.9. At this pH the Ca^{++}/H^{+} exchange reaction was markedly reduced, consequently a little change in the surface composition of the FA powder could be expected.

3.3 Casting rate of suspensions and microstructure of the consolidated bodies

Slip casting is the formation of a consolidated layer, or cake, on the surface of a porous body (11). During this process, a dry porous mold contacts a suspension and the porous surface is wetted by the suspension. The capillary suction caused by the porous mold drives ceramic particles to concentrate at the mold-suspension boundary, and a wet cake is formed if the particles cannot enter into the pores (11). Fluid flow through the consolidated layer and into the porous body is governed by the Darcy's law, which express the variation of the layer thickness, h, as a function of time, t :

$$h=2(\varepsilon_n \gamma K t /\eta \alpha R_n)^{1/2}$$
 (D)

where K is the permeability of the wet cake, η is the viscosity of the liquid, R_n is the pore radius of the mold and ε_n its porosity, γ represents the surface tension of the liquid in the pores of the mold and α is defined as (ϕ_0/ϕ) -1 (ϕ_0 and ϕ are the volume fraction of particles in the suspension and in the wet cake, respectively). In this work, the porosity and the pore diameter of the mold were fixed, therefore the cake formation rate depended on the pore structure of the wet cake and the viscosity of the fluid.

Figure 4 shows the layer thickness square as a function of time for stabilized 38 vol.% slips with 0 and 0.5 wt% PVA. At the beginning (60 min), a greater casting rate of the slip without PVA with respect to that with PVA was found, resulting in an increase of the layer thickness. This was attributed to the lower viscosity of the fluid without PVA which increased the initial liquid flow through the porous mold. Once the cake was growing (t> 60 min), the casting rate of the slip without PVA was significantly lower resulting in a reduction of the layer thickness at a given time.

In order to explain the difference between the h^2 vs. t curves the pore structure of the resultant green cakes were examined. Figure 5 shows the cumulative micropore volume by mass unit versus pore radius curves of cakes obtained from slips with 0 and 0.5 wt% PVA. An unimodal distribution of pore sizes was observed for both samples, the most frequent pore radius were 0.02 and 0.03 µm for the cakes produced from slips with 0 and 0.5 wt% PVA, respectively. A greater volume of pores and pore size were found for the cake obtained from the slip with PVA (Fig. 5). The greater permeability of these cakes increased the casting rate; thus, for t>60 min when the cake was growing, the casting rate was governed by its permeability.



Figure 4: Layer thickness square as a function of time for stabilized 38 vol.% slips with 0 and 0.5 wt% PVA.



Figure 5: Cumulative micropore volume by mass unit versus pore radius curves of cakes prepared from slips with 0 and 0.5 wt% PVA.

Table 1 lists the relative viscosity values of the suspensions with 0 and 0.5 wt% PVA at a shear rate of 126 s⁻¹, together with the density of green and sintered bodies. The lower viscosity values of slips without PVA produced green bodies with higher densities; this was consistent with the lower volume of pores found after slip casting (Fig. 5). In these slips the particles could pack in an ordered way due to the repulsive forces existing between them, resulting in high green densities of slip cast bodies.

Table 1

Relative viscosity of 38 vol.% stabilized suspensions with 0 and 0.5 wt% PVA and properties of the consolidated bodies

Sample	Slurry relative viscosity	Green density	Sintered density
	(at γ= 126 s⁻¹)	(%TD)	(%TD)
0 wt% PVA	11.8	61.5	97
0.5 wt% PVA	58.8	57.0	95

The addition of PVA promoted aggregation of particles increasing the slip viscosity; consequently, compacts with lower green densities were obtained. Sintered densities of 95 and 97 % of the theoretical density (TD) were achieved for the bodies obtained using slips with 0.5 and 0 wt% PVA, respectively. There was a close relation between green and sintered densities, the less dense materials produced from slips with PVA were attributed to the less particle packing achieved in the green bodies (table1).

4. CONCLUSIONS

The surface reactivity of fluorapatite in an aqueous solution with and without dispersant was investigated. An initial release of F anions located at the surface was found, which was not dependent of the initial pH of the solution and the presence of dispersant. The increase in the initial pH of the solution above 7 and/or the presence of NH₄PA markedly reduced the Ca⁺⁺/ H⁺ exchange reaction rate. The addition of FA to an aqueous solution with NH₄PA in weakly alkaline conditions (pH ~9) produced the lowest decrease in pH, consequently the Ca and P removal and the up take of H⁺ via proton-Ca exchange reaction were minimized.

The high viscosity values of the slips with PVA promoted the formation of more porous green microstructures and lower densities of slip cast bodies. The greater permeability of these cakes also increased the casting rate.

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