

Hydroxyapatite Physical-Chemistry Relationship: Crystallite Dimension X In Vitro Degradation Rate

F. J. C. Braga¹, V. L. R. Salvador¹, L. G. Martinez¹, C. R. Meira², G. G. Prado²,

(1) Instituto de Pesquisas Energéticas e Nucleares (IPEN) – Av. Prof. Lineu Prestes, 2242, São Paulo, SP, Brazil

(2) Consulmat Ltda. – Rua Juan Lopes, 159, São Carlos, SP, Brazil

fjcbra@ipen.br

Introduction.

The materials utilized as bone graft point out the compound of HYDROXYAPATITE ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) as the most used in dental surgery. The critical attention of the surgeons to this material, is related to the material capability or not to be resorbable by the organism. This is suitable to specific cases where in one side the target is the bone regeneration process substituting the biomaterial by new tissue to be formed, or by the other side, the purpose is to remain it definitely in defective site as an osteoconductor charge. In this way, the physical-chemistry properties of the biomaterial are very important to correlate the response and capacity to resist to the organism aggression.

Materials and Methods.

The former hydroxyapatite was chemically obtained from bovine bone without any thermal process to avoid modifications in its original crystallite size. After this step, the powdered hydroxyapatite was thermally treated by one hour at 700°C, 900°C and 1100°C. The classification of particle surface area was measured by BET method. The hydroxyapatite chemical composition was presented by WDXRF and the phase identification was obtained by comparison XRD spectra with ICDD-PDF database. The Rietveld refinement of XRD data was performed using the program GSAS. The crystallite size determinations were done by means of Scherrer equation. The *in vitro* biodegradation test was realized in citric acid buffer solution with a pH 4,3 at 40°C during 10, 20 and 30 days, where samples of the solution were collected after each these periods to be analyzed by WDXRF on its Ca^{++} content.

Results and Discussion.

The Table I show the chemical composition of the material through its oxides percentages. The Ca/P relationship is a little bit higher the ideal value (1,67) possibly due to the presence of those detected impurities. The particle surface area value of the material is $221,6 \pm 0,2558 \text{ m}^2/\text{g}$.

Table I - Chemical composition of hydroxyapatite.

Compounds	CaO	P ₂ O ₅	SrO	ZnO	Fe ₂ O ₃	ZrO ₂	Ca/P
%	58.764	41.147	0.057	0.020	0.010	0.002	1.81

The Table II shows the results of Rietveld refinements of XRD data and the values of crystallite size for the samples.

Table II - Results of Rietveld refinements and crystallite size.

PARAMETERS	ORIGINAL	700 °C	900 °C	1100 °C
Mean Cryst Size (nm)	20,6	24,1	39,2	47,4

The Figure 1 shows the amount of Ca^{++} dissolved in the citric acid buffer solution. The values of Ca^{++} determined by linear regression method are in the Table III. A theoretical curve obtained by the exponential growth regression from experimental data of crystallite size is shown in the Figure 2.

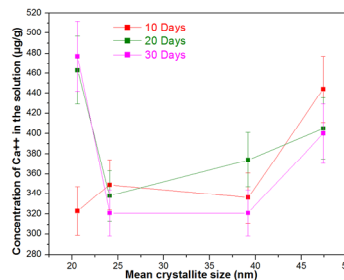


Figure 1 - Concentration of Ca^{++} in the solution originated from the Hydroxyapatite with four crystallite sizes, per each period of dissolution.

Table III - [Ca^{++}] from the samples in the buffer solution.

SAMPLE	10 DAYS	20 DAYS	30 DAYS
Original (Ca^{++} µg/g)	323±24	463±34	477±35
700 °C (Ca^{++} µg/g)	349±25	338±25	321±23
900 °C (Ca^{++} µg/g)	336±25	374±27	366±27
1100 °C (Ca^{++} µg/g)	444±33	405±30	400±29

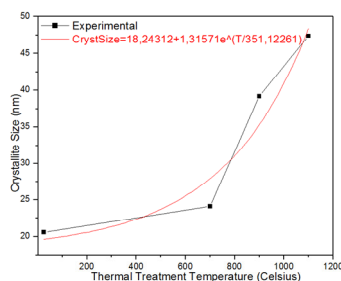


Figure 2 - Crystallite size versus temperature of treatment.

The crystallite size can correspond to the subgrain size existing in the grains of the material, where the higher is its size less quantity of boundaries and consequently lower is the free energy of the grain. So, it is reasonable to consider that to higher is the crystallite size, more energy should be done to the material be dissolved. Unfortunately, to the analysed crystallite size range, the dissolution of Ca^{++} suggest be the same after the test period of 10 days. The questioning of possible phase changes in the material during the thermal treatment is rejected due to: (a) no additional peaks were observed in the XRD spectra of thermally treated samples comparing with the original one; and (b) the calculated lattice parameters by GSAS program did not show significant changes in value defining in all the samples the same crystalline system, e. g., hexagonal system.

Conclusions.

- The mean crystallite size of the hydroxyapatite treated from 700 °C to 1100 °C increases in 130%;
- The [Ca^{++}] in the citric acid solution from 20 to 30 days is higher to the original sample;
- The [Ca^{++}] in the citric acid solution shows no clear relationship with the mean crystallite size from 24.1nm to 47.4nm range but suggests a tendency of a direct relationship.