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Synthesis of the apatite with a blend of the powder of calcite

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ABSTRACT

We have studied the influence of residence time in a humid atmosphere on the synthesis of apatitic phosphate calcium. The initial atomic ratio of calcium to phosphorus Ca/P is constant and equal to 1.00 ± 0.01 . The XRD analysis has shown the formation of a poorly crystalline calcium phosphate with an apatitic structure. Beyond 48 hours only the hydroxyapatite phase was found. For cons, a treatment of a mixture during the residence time that is less than 48 hours led to the formation of a mixture of hydroxyapatite and calcium carbonate (calcite). Similarly, the infrared absorption spectroscopy for short residence times ranging from 2h to 8h still shows the presence of bands due to ions CO_3^{2-} specific calcite that decrease by increasing the residence time. Beyond a residence time of 48 hours there was a total disappearance of these band and chemical analysis by the atomic shows that the ratio Ca/P remains practically constant and equal to 1.60 ± 0.01 . © 2012 Trade Science Inc. - INDIA

INTRODUCTION

The calcium orthophosphates are the mineral part in the human hard tissues (bone of teeth)^[1]. So, the synthesis, the structure and the reactivity of this chemical element have received of many basic studies. Also, these phosphates are presented in form of the apatite.

The apatites are a family of compounds isomorphous chemical formula $\text{ME}_{10}(\text{XO}_4)_6\text{Y}_2$ where Me represents a divalent cation (Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} ...), XO_4 an anion trivalent (PO_4^{3-} , VO_4^{3-} , AsO_4^{3-} ...) and Y a monovalent anion (OH^- , Br^- , Cl^- ,...).

Their structure is characterized by the existence of tunnels where are located the Y-ions. The presence of these tunnels provides a remarkable mobility to the ions they contain and allows easy substitutions within the network^[2].

The substitution of trivalent ions XO_4^{3-} by divalent ions such as CO_3^{2-} , HPO_4^{2-} is also possible. The balancing of charges takes place thanks to the creation

of gaps. He then leads to a deficient in the apatite, poorly crystallized, similar to those found in the calcified tissue of bones and teeth. The apatites thus obtained have the following formula^[3]:



Various methods have been developed for the synthesis of calcium phosphates. Two main types of reactions of preparation are generally used, the reactions in aqueous phase (wet) and solid phase reactions (in dry).

The wet process can be divided into hydrothermal precipitation and hydrolysis of other calcium phosphates^[4].

The hydrothermal method was used for the first time in the development of hydroxyapatite from natural calcite aragonite variety^[4].

Currently the hydrothermal process is used in the industrial synthesis of apatitic calcium phosphate. This treatment is in most cases to be treated under steam in a closed chamber, a reactant mixture at a temperature

Full Paper

between 100 °C and 500 °C and a pressure of water vapor from 0.5 to 17 MPa. This treatment can take place in the autoclave to handle according to two methods:

- The mixing of the reactants is totally immersed in the aqueous medium so that it is in contact with water in liquid form. This first process leads to the preparation of apatite by hydrothermal treatment at temperatures between 160 °C and 200 °C in solution of a mixture of CaCO_3 and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in aqueous basic (pH = 10).

- The mixing of the reactants is deposited above the liquid medium so that it is in contact with water vapor produced under the effect of temperature. This synthesis method was used to prepare the hydroxyapatite from marine algae, which are characterized by its high rate (80%) of calcium carbonate CaCO_3 and the presence of a phosphate salt^[5].

However, the physico-chemical properties of calcium phosphates mainly depend on their molar ratio Ca/P, which in turn is directly related to the chosen operating conditions during the synthesis.

Thus, we seemed interesting to study the synthesis of calcium phosphates by hydrothermal method using powder mixtures of calcium salt and phosphate salt, but in other experimental conditions in order to promote the formation of a phosphate non-stoichiometric calcium apatite. The behaviour of the mixture of reagents was followed over time in an autoclave at a temperature below 100 °C (80 °C) and in a saturated water vapor (100% humidity)^[6].

MATERIALS AND METHODS

The calcium salt and phosphate salt that we used in this study are the calcite (CaCO_3 , Prolabo) and the salt of di-ammonium hydrogen phosphate ($(\text{NH}_4)_2\text{H}_2\text{PO}_4$, Prolabo). An initial mixture of powdered calcium to phosphorus which has an atomic ratio Ca/P equal to 1.00 ± 0.01 was homogenized by grinding and then placed in an autoclave under a humid atmosphere.

The device used to study the behavior in humid mixtures of salts and calcium phosphate (Figure-1) consists of a reactor placed in a chamber at 80 °C (100% humidity). The reactor contains water to saturate the atmosphere. 27.36 ± 0.01 mg of the powder was

spread in watch glasses in the reactor and stored for times ranging from hours to days.

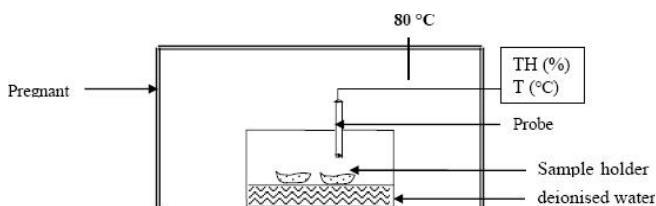


Figure 1: Experimental device

After fixing of the residence time, the samples were removed from the chamber and dried for 1 hour at the temperature of the study. This precaution was taken to prevent further development of the product due to the presence of water adsorbed on the surface. Then the samples were washed on a sintered glass twice with distilled water and three times with a solution of water-ethanol (50/50 by volume) and dried in an oven for 4 hours. The products recovered from these conditions were calcined at 900 °C in air for two hours. To monitor changes over time, the samples recovered after washing were characterized by X-ray diffraction using a diffractometer "XPERT-PRO" (Cobalt=1,54439 Å). The crystallite size was estimated from the width of XRD lines according to SHERRER formula^[7]. The characterization by infrared absorption spectroscopy was performed in the interval 400 cm^{-1} - 4000 cm^{-1} , with a Bruker spectrometer. By IR analysis, approximately 1 mg of powder was carefully ground with 200 mg of potassium bromide KBr powder in a mortar agatat. Transparent pellets were obtained under a pressure of 15 mbar.

Examinations by electron microscopy (SEM) of the recovered powders after washing powders were performed on a microscope that allows high-resolution observation and, equipped with a complete X-ray microanalysis (EDX-EDAX detector), it can give the chemical composition of the sample with a detection limit up to Bore.

The calcium and phosphate ions were determined on samples recovered after washing, by chemical analysis.

The calcium was assayed in return. The complexing agent is EDTA in the presence of ammonia. The excess of EDTA used is then determined by a solution of ZnCl_2 .

The phosphate is present in the solid form of group studied HPO_4^{2-} and PO_4^{3-} . It was determined by colo-

rimetry at 460 nm. The principle of this method is to measure the optical density of the yellow complex molybdovanadate phosphorus in acid medium.

The ions of hydrogen- HPO_4^{2-} were assayed after treatment of samples at 600°C during 20 minutes. During of this heating HPO_4^{2-} ions condense to give pyrophosphate $\text{P}_2\text{O}_7^{4-}$ ions according to:



The orthophosphate ions from heated material were measured after acid hydrolysis at 100°C during 1 hour. The amount of phosphorus in the form of ion- HPO_4^{2-} was obtained by the difference between the amounts of phosphorus determined before and after hydrolysis^[8].

RESULTS

The study of behavior under a moist atmosphere of powder mixtures initial with atomic ratio Ca/P equal to 1.00 ± 0.01 was monitored as a function of time ranging from 2 days to 21 days.

Analysis by infrared spectroscopy

The infrared absorption spectra of mixtures treated in a humid atmosphere as a function of residence time at 80°C are shown in Figure 2. These spectra show well-defined bands that can be easily identified from their wave numbers.

In short residence times ranging from 2 hours to 8 hours, there was always the presence of bands due to ions CO_3^{2-} specific calcite located at 712 cm^{-1} at 1420 cm^{-1} and 1480 cm^{-1} ^[9]. Also, It appears next to those of calcite bands located at 474 cm^{-1} , 571 cm^{-1} , 602 cm^{-1} , 960 cm^{-1} , 1046 cm^{-1} and 1088 cm^{-1} and 875 cm^{-1} characteristics of groups 1 PO_4^{3-} and HPO_4^{2-} in a non stoichiometric apatite^[10]. The total disappearance of the bands of calcite is observed for a residence time of 48 hours. Beyond this time, the infrared absorption spectra are similar to those of calcium phosphate apatite deficient calcium ions.

Indeed, the spectra reveal also that the decrease in residence time decreased the intensity of the bands HPO_4^{2-} ions and a gradual increase of bands characteristic of OH^- ions located at 3560 cm^{-1} and 630 cm^{-1} .

These observations show that, depending on residence time, an evolution of the initial powder mixtures

in a humid atmosphere, to a more stoichiometric apatite.

Moreover, the infrared absorption spectrum of the treated sample in a humid atmosphere for 21 days, then calcined at 900°C (Figure 2 (e)) shows the presence of bands, respectively, characteristics of groups PO_4^{3-} and OH^- in hydroxyapatite calcium phosphate, and those located at 985 cm^{-1} features ion PO_4^{3-} tricalcium phosphate β ^[10].

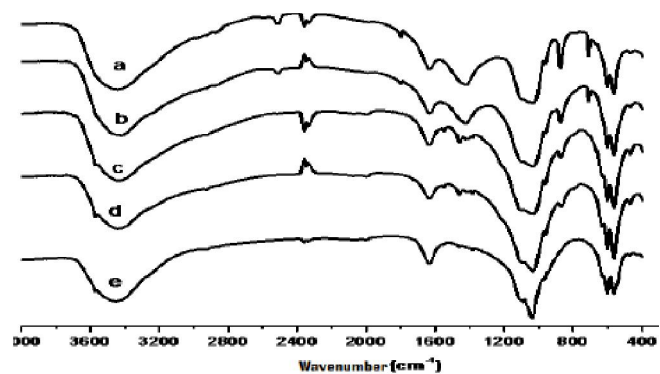


Figure 2 : Infrared absorption spectra of samples treated in a humid atmosphere as a function of residence time: (a) 2 hours, (b) 8 hours, (c) 48 hours, (d) 21 days, (e) and 21 days at 900°C

Analysis by X-ray diffraction

The X-ray diagrams of samples recovered after treatment in the conditions described above, the atomic ratio of calcium to phosphorus Ca/P equal to the initial 1.00 ± 0.01 are shown in Figure 3.

Analysis by X-ray diffraction leads to the same results as previously revealed by infrared spectroscopy. After 2 hours, one detects a mixture of calcite and apatite in a poorly crystallized^[11, 12]. Calcite was identified by the presence of particular diffraction line at its $d_{104} = 3.035\text{ \AA}$.

When the residence time increases, the apatitic phase becomes dominant ; the crystallization of the apatite is getting better and the stripes (002), (211), (112) and (300) are more refined^[12]. The crystallite size was calculated from the width at half height of the line (002) of apatite is reported in TABLE 1. It is found that the crystallite size increases from 626.24 \AA to 852.88 \AA after 21 days

Moreover, the X-ray diagram of the product having stayed 21j then calcined at 900°C shows the lines corresponding to two phases: the calcium phosphate hydroxyapatite^[12] and phosphate tricalcique- β (214),

Full Paper

(0210) and (220)^[13].

TABLE 1 : Crystallite size as a function of residence time.

Time	2 hours	8 hours	48 hours	21 Days
Crystallite sizes in Å	626,24	633,46	816,44	852,88

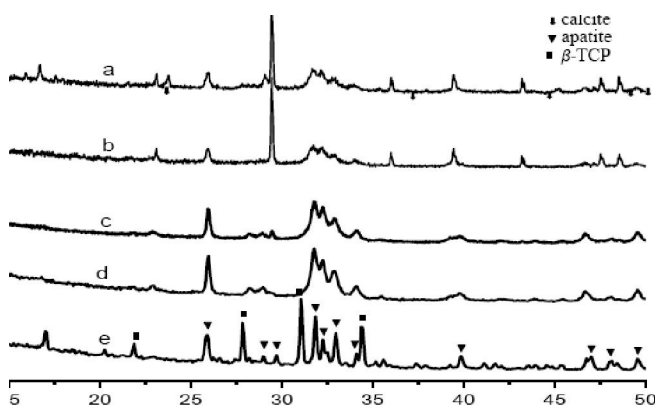


Figure 3 : Diagram of X-ray diffraction of samples processed in a humid atmosphere as a function of residence time: (a) 2 h, (b) 8 hours, (c) 48 hours, (d) 21 days and (e) 21 days to 900 °C

Scanning electron microscopy

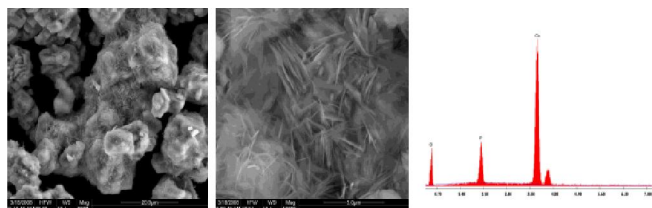


Figure 4 : Snapshots obtained by scanning electron microscopy of the mixture of initial atomic ratio Ca/P = 1.00 ± 0.01 after treatment for 21 days at 80 °C.

The photographs obtained by scanning electron microscopy have revealed the presence of a phase consisting of a cluster of needles.

Study by chemical analysis

To determine the chemical composition of products obtained, the levels of calcium ions and ortho-phosphate were determined on samples recovered after different residence times and after their washing (TABLE 2).

TABLE 2 : Changes in atomic ratios of the samples before and after reaction.

Time	0 hours	2 hours	4 hours	8 hours	24 hours	48 hours	3 days	7 days	21 days
Ca/P	1,00	2,42	1,72	1,71	1,58	1,58	1,59	1,60	1,60
%HPO ₄ ²⁻ / P _i	—	6,05	10,49	13,20	9,32	8,80	6,70	6,37	5,63
IR	CaCO ₃ + (NH ₄)H ₂ PO ₄	Apatite+CaCO ₃	Apatite+CaCO ₃	Apatite+CaCO ₃	Apatite+CaCO ₃	Apatite	Apatite	Apatite	Apatite
DRX	CaCO ₃ + (NH ₄)H ₂ PO ₄	Apatite+CaCO ₃	Apatite+CaCO ₃	Apatite+CaCO ₃	Apatite+CaCO ₃	Apatite	Apatite	Apatite	Apatite

We note that the Ca/P ratio of initial mixtures increases by length of stay from the value of 1.00 ± 0.01 to 1.71 ± 0.01 after 8 hours. As was revealed by IR and XRD, this increase is mainly due to the simultaneous presence of two phases calcite and non stoichiometric apatite. Moreover, beyond 48 hours, the Ca/P ratio remains practically constant and equal to 1.60 ± 0.01 after 21 days.

The observations made by different analytical techniques have allowed us to distinguish the formation of an apatite. The X-ray diffraction and infrared absorption spectroscopy indicate that these phosphates have a apatitic structure. On the other hand, the latter technique reveals the presence of PO₄³⁻ ions and OH⁻ ions, and the existence of ion-HPO₄²⁻ belonging to the apatite phase.

In addition, chemical analysis of elements show that beyond 48 hours, the apatitic calcium phosphates formed are made only of Ca²⁺, PO₄³⁻, HPO₄²⁻ and OH⁻. The chemical formulas of apatite obtained were established from the chemical analysis and are reported in TABLE 3.

TABLE 3 : The chemical formula of apatites synthesized in a humid atmosphere at different residence times.

Time	Chemical formula
48 hours	Ca _{9,47} (PO ₄) _{5,47} (HPO ₄) _{0,53} (OH) _{1,47}
3 days	Ca _{9,59} (PO ₄) _{5,59} (HPO ₄) _{0,41} (OH) _{1,59}
7 days	Ca _{9,61} (PO ₄) _{5,61} (HPO ₄) _{0,39} (OH) _{1,61}
21 days	Ca _{9,66} (PO ₄) _{5,66} (HPO ₄) _{0,34} (OH) _{1,66}

INTERPRETATIONS AND DISCUSSION

We have prepared the initial powder mixtures between the salts of calcium carbonate CaCO₃ and ammonium dihydrogen phosphate [(NH₄)H₂PO₄] that have an atomic ratio Ca/P constant and equal to $1.00 \pm$

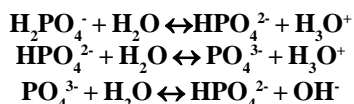
0.01. The behavior in a humid atmosphere was studied to clarify the influence of residence time on the products obtained.

The study by X-ray diffraction and infrared absorption spectroscopy at different residence times exceeding 48 hours has given a same result. It show the formation of a poorly crystalline calcium phosphate and a apatite structure. The spectra of samples recovered have revealed the presence of bands characteristic groups PO_4^{3-} and HPO_4^{2-} in a non-stoichiometric apatite^[10-14]. These results reflect that in atmosphere saturated with water vapor, an evolution of the initial mixtures to the deficient apatite of calcium ions. In addition, the state of crystallization improves when the treatment time increases. Also, it should be noted that the presence of calcite in the samples treated for residence times less than 48 shows that the reaction between CaCO_3 and $(\text{NH}_4) \text{H}_2\text{PO}_4$ in a humid atmosphere depends primarily on the residence time.

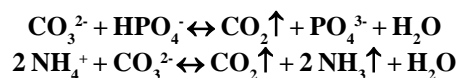
By chemical analysis, the concentrations of Ca^{2+} , PO_4^{3-} and HPO_4^{2-} were determined and the atomic ratio Ca/P was calculated. The study of changes in atomic ratios showed us that the atomic ratio Ca/P phosphate remains constant without significant change, despite the increased length of stay.

In addition, the variation rates of HPO_4^{2-} ions shows a progressively decrease when the processing time of the initial mixture in a humid atmosphere increases.

This variation in the rate of ion HPO_4^{2-} is certainly due to the balance that to be established between the reagents. Indeed, in infrared absorption spectroscopy, there was an increase the intensity of the bands associated with OH^- ions. Thus, as has been repeatedly shown^[15], it is possible to admit that the OH^- ions observed from the hydrolysis intercrystalline phosphate ions in the formation of apatite came as result of :



Similarly the chemical analysis reveals a significant loss of ions CO_3^{2-} and NH_4^+ of the initial mixture. This loss of ions accompanied by the disappearance of H_2PO_4^- ions, is performed, most likely, according to the following reactions:



In these conditions, it appears that the synthesis of calcium phosphate apatitic structure is due to hydrolysis of the species found in the initial mixture. This reaction is probably favored by the saturated water vapor and a priori this medium of exchange can not be the film that formed on the surface of powders of the salts.

In addition, changes in calcium phosphates occurs in most cases in solution or by a mechanism of dissolution- reprecipitation^[6, 10, 16, 17] or by a topotactic mechanism^[17-19].

Conceivably, in our experimental conditions, the important role of adsorbed water film on the initial decomposition of mixtures of salts in a humid atmosphere in apatite. Therefore the reaction mechanism can be envisaged in two stages: dissolution of some ions of the initial mixture to the surface by the adsorbed water film. Once the saturation condition is achieved, there may be a nucleation (or germination). This step in the crystallization process is necessary to the formation of germs of sufficient size allowing subsequent growth. The nucleation process can occur either homogeneously or heterogeneously in the presence of foreign particles that act as nucleation sites^[20-22]. In our case, the model of homogeneous nucleation was chosen for the single-phase samples are recovered and no foreign phase was detected.

CONCLUSION

The method of hydrothermal synthesis as a function of residence times that we presented in this work led us to the preparation of a calcium phosphate apatite that is deficient in calcium ion and has an atomic ratio equal to $1.60 \pm 0, 01$ similar to that of the mineral part of calcified tissues^[2].

The result has shows that the characterization of the product treated during 21 days and then calcined at 900 °C, XRD and IR in a humid atmosphere shows an evolution of initial salts to a biphasic apatite consisting of calcium phosphate hydroxyapatite and tricalcium phosphate β .

Also, by chemical analysis, beyond 48 hours, the Ca/P ratio remains practically constant and equal to 1.60 ± 0.01 .

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