



Synthesis and Characterization of New Copper(II) Substituted Dicalcium Phosphate Dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$)

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We have investigated, in aqueous solution, the exchange process of calcium by copper ($\text{Ca}^{2+}/\text{Cu}^{2+}$) and its effects on the chemical and structural stability of dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). The compounds obtained at different concentrations of Cu^{2+} and various pH were characterized by X-ray diffraction, spectroscopically, chemical analysis and SEM-EDS microscopy. The combined results of these methods, confirmed that copper ions incorporate partially the dicalcium phosphate dihydrate framework by the exchange of Ca^{2+} ions with copper favouring the formation of $\text{Ca}_{1-x}\text{Cu}_x\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ solid solution which is isomorphic to the pure dicalcium phosphate dihydrate. The upper limit of copper solubility in dicalcium phosphate dihydrate is observed at 25 %. Unlike calcium, Cu^{2+} ions prefer to be hosted by low symmetry sites in dicalcium phosphate dihydrate structure causing a slight compression of the unit cell. This exchange inhibits the nucleation of derived hydroxyapatite compounds frequently observed with many other divalent cations. The dehydration in air at 250 °C of dicalcium phosphate dihydrate - % Cu^{2+} can lead to the formation of stable anhydrous products $\text{Ca}_{1-x}\text{Cu}_x\text{HPO}_4$ (DCPA) with monetite structure.

Key Words: Calcium phosphate, Copper-calcium phosphate, Exchange reaction synthesis.

INTRODUCTION

The calcium-phosphate system belongs to a class of materials extremely attractive because of the large variety of the structures and the compositions^{1,2}. The materials such as calcium-hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, CaHAp], tricalcium phosphate [$\text{Ca}_3(\text{PO}_4)_2$, β TCP] and dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, DCPD) have several applications in the biomedical technologies. They are the inorganic constituent of bones and teeth enamel and are of great utility in bioceramics. Their biocompatibility has been confirmed in *in vitro* and *in vivo* studies^{3,4}. Moreover, many phosphates of the same family were investigated in heterogeneous catalysis, particularly in the oxidative dehydrogenation of alkanes, the conversion of alcohols, hydration of chlorobenzene and hydroxylation of aromatics⁵⁻⁸. Depending on the nature of the incorporated metallic cation they might exhibit good catalytic performance and selectivity equivalent to that achieved with apparent materials^{9,10}.

Nevertheless, this class of materials is one of the most complex families of the phosphates probably because the chemical stability of most of the compounds is not only affected by the Ca/P atomic ratio but also by the factors that determine the kinetics of synthesis reaction such as the

temperature, the pH of precipitation, the nature of the precursors and the complexing agents^{11,12}.

Recently, much effort has been devoted to the improvement of the characteristics of dicalcium phosphate dihydrate $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (DCPD). New nano-composite biomaterials were produced and isolated by including to the synthesis media an inert organic matrix such as cellulose, polyester or chitosan¹³⁻¹⁵. The dicalcium phosphate dihydrate was also proven to be the precursor in the precipitation of calcium-hydroxyapatite in physiological conditions. It is the most stable phase of calcium-phosphate system in acidic media. The incorporation of metallic cations such as Mg^{2+} , Co^{2+} , Zn^{2+} and Fe^{2+} play a major role in promoting or inhibiting the formation of calcium-hydroxyapatite starting from dicalcium phosphate dihydrate. Those cations generally improve the crystal growth of calcium-hydroxyapatite (CaHAp). They also enhance the expansion of the size and the morphology of the phosphates deriving from CaHAp¹⁶⁻¹⁸. As reported, all preparations of dicalcium phosphate dihydrate-% M^{2+} were conducted using the direct synthesis and to our best of knowledge no study has been carried out by ion exchange process.

The present work reports the synthesis of new copper(II)-calcium mixed phosphates (DCPD-% Cu^{2+}) by soft chemistry and at low temperature. The isolated compounds, at several

experimental conditions were characterized by X-ray diffraction, spectroscopic techniques (IR, UV-Visible) and SEM-EDS microscopy. The attempt was to synthesize new catalyst formulations which could be a good candidate in liquid phase reactions catalysis.

EXPERIMENTAL

Samples preparation: The copper-calcium mixed phosphate (DCPD-% Cu²⁺) containing different concentrations of Cu²⁺ was prepared at room temperature using the batch method. One gram of commercial CaHPO₄·2H₂O (99 %, Riedel-de Haën) was introduced into 100 mL of a copper nitrate Cu(NO₃)₂·3H₂O (99.2 %, Merck) solution at Cu/(Cu+Ca) molar percentage ranging from 0 to 60 %. The reaction was carried out at a controlled pH while the solution was kept for 5 h under stirring. The obtained suspension was filtered, then washed and dried in air before being placed overnight in an oven at 60 °C. Few samples of dicalcium phosphate dihydrate-% Cu²⁺ were calcined for 24 h at different temperatures in order to examine their thermal stability. The colour of all the samples is a more or less pronounced dark blue depending on the amount of copper contents.

Characterization: The copper/calcium molar ratio of all the prepared products was determined by elemental analyses using an inductive coupling plasma-atomic emission spectroscopy ICP-AES (Jobin Yvon, Ultima 2). The copper remaining in the solutions after the filtration was analyzed by colourimetry using GBC 911 UV-VIS spectrophotometer.

The compositions of the phases were studied by X-ray diffraction (XRD) at room temperature on a Philips PW 3050/60 X'pert Pro diffractometer with CuK_α radiation (40 kV, 30 mA). The XRD data were collected over the 2θ range from 5 to 60° with step size of 0.02°. The identification of the phases and the refinement of the cell parameters were performed using structural models of ICDD database.

The FTIR analyses of dicalcium phosphate dihydrate-% Cu²⁺ were carried out at room temperature between 400 and 4000 cm⁻¹ using an IRTF Vertex 70 spectrometer and the KBr pellet technique.

UV-Visible diffuse reflectance spectra (DRS) of the samples containing copper ions were recorded at room temperature between 200 and 1400 nm on a Perkin-Elmer spectrometer (UV/Vis Lambda 900). The spectra were collected using BaSO₄ reflectance as the base line reference. Pure dicalcium phosphate dihydrate phosphate was used for comparison. The morphology and the texture of the samples was studied by scanning electron microscopy (SEM) using a Cambridge Stereoscan 120 instrument coupled with chemical analysis (EDS).

RESULTS AND DISCUSSION

Effect of pH copper solution on dicalcium phosphate dihydrate: Fig. 1 shows the changes of the initial and final pH of the copper solution before and after the addition of 1 g of dicalcium phosphate dihydrate. The pH of the solutions at equilibrium decreases rapidly when the concentration of Cu²⁺ ions is increased. This decrease becomes more noticeable when the Cu/(Cu+Ca) molar percentage exceeds 25 %. Above this

value and at the pH which gradually decreases, a mass loss of the final product is observed and is due to partial dissolution of dicalcium phosphate dihydrate in aqueous phase.

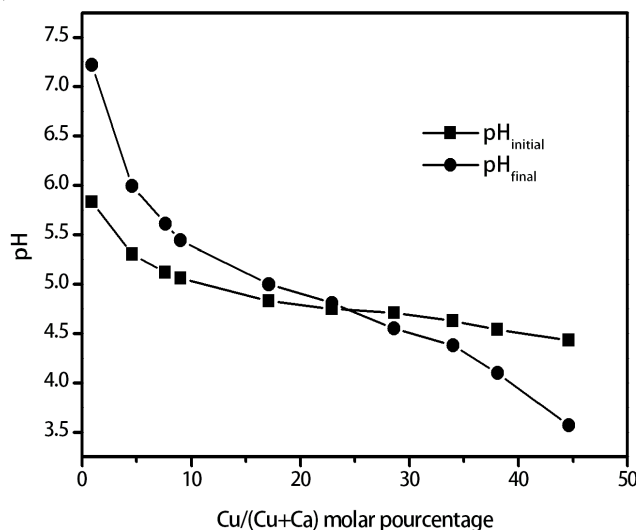


Fig. 1. Behaviour of initial and final pH of the copper solution after the addition of dicalcium phosphate dihydrate

Stoichiometric analysis: The copper and calcium analyses in dicalcium phosphate dihydrate-% Cu²⁺ and pure dicalcium phosphate dihydrate are displayed in Fig. 2. The results show noticeable differences between the experimental and the theoretical values of Cu/(Cu+Ca) molar ratios, before and after reaction. For copper content below 25 %, the concentration of calcium ions decreases gradually in the dicalcium phosphate dihydrate products with the increase of copper ions, suggesting that the substitution of Ca²⁺ by Cu²⁺ ions did take place. The reaction seems globally to be dominated by ion exchange process between Ca²⁺ in the materials and aqueous Cu²⁺. For copper concentrations greater than 25 %, the pH of the solutions decreases intensely and the amount of copper measured becomes progressively larger than expected. Concomitantly, abnormal loss of calcium was observed. In this case, a new chemical process appears. It's attributed to the dissolution-precipitation mechanism of the dicalcium phosphate dihydrate phosphate which can be occurs between the entities [HPO₄]²⁻ released by the partial dissolution of dicalcium phosphate dihydrate and the precipitation of an extra phase containing only copper-phosphate in the presence of Cu²⁺ ions.

XRD analysis: The X-ray diffraction patterns of dicalcium phosphate dihydrate-% Cu²⁺ compared with the pure dicalcium phosphate dihydrate are displayed in Fig. 3. They show a slight shift in the principal reflections toward larger angles when the copper content in solution is increased. Probably, because the copper ions Cu²⁺ (0.62 Å) are partially incorporated into the dicalcium phosphate dihydrate lattice thus replacing Ca²⁺ (0.99 Å) cations which are larger. Similar results were obtained by Guerra-lopez¹⁹ in studying the incorporation of nickel in the same phosphate matrix.

The computed lattice parameters are presented in Table-1. They reveal a decrease of lattice constants confirming the substitution of Ca²⁺ ions by Cu²⁺ in the framework. Moreover,

for Cu/(Cu+Ca) molar percentage exceeding 25 %, extra peaks appear in the diffractogram at $2\theta = 7.55^\circ$ and 12.4° , which rises gradually when the amount of copper is increased. They can be attributed to the nucleation and crystallization of a new phosphate phase containing only copper ions which having a chemical formulation similar to $\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. This copper phosphate is less known in the literature, although already reported²⁰.

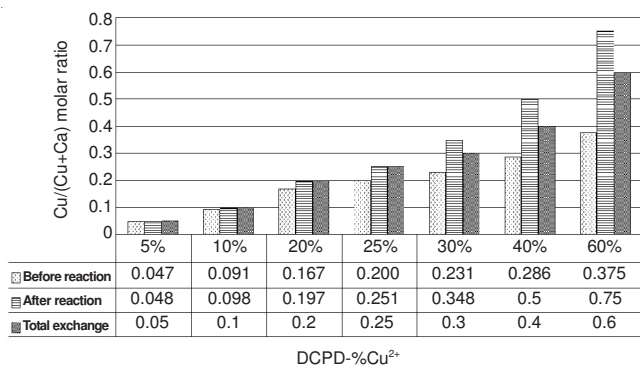


Fig. 2. Elemental analysis of pure dicalcium phosphate dihydrate and dicalcium phosphate dihydrate- % Cu^{2+}

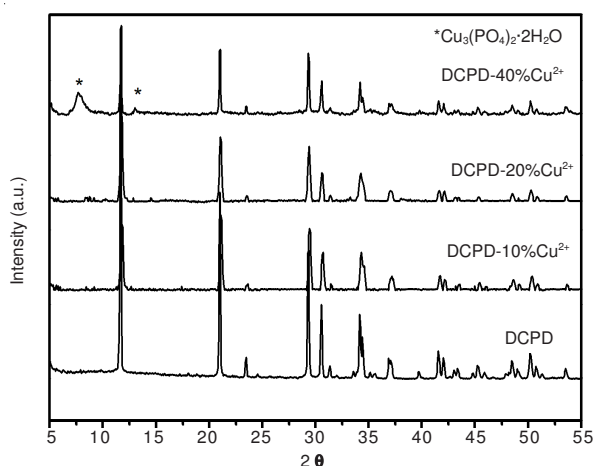


Fig. 3. XRD patterns of pure dicalcium phosphate dihydrate and dicalcium phosphate dihydrate- % Cu^{2+} samples

Lattice constant	Pure DCPD	DCPD-10 % Cu^{2+}	DCPD-20 % Cu^{2+}	DCPD-30 % Cu^{2+}
a(Å)	5.838(4)	5.821(3)	5.815(3)	5.807(3)
b(Å)	15.191(6)	15.168(6)	15.134(7)	15.129(5)
c(Å)	6.265(5)	6.237(5)	6.218(5)	6.215(4)
β°	116.47	116.28	116.09	116.15
V(Å ³)	497.36	493.76	491.45	490.13
Symmetry	Monoclinic	Monoclinic	Monoclinic	Mixture

According to the chemical analyses results reported above and to the XRD diagrams, the ion exchange between calcium and copper in the dicalcium phosphate dihydrate- % Cu^{2+} leads to a crystallized phase limit whose chemical formula, is very close to $\text{Ca}_{0.75}\text{Cu}_{0.25}\text{HPO}_4 \cdot 2\text{H}_2\text{O}$. Above this limit, the obtained compounds are biphasic. They consist of the limit solid solution

of copper-calcium-phosphate and the pure copper phosphate $\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. In our chosen experimental conditions, no other phases were observed. It seems that the copper, like some other divalent ions, acts as a stabilizer of the dicalcium phosphate dihydrate by inhibiting its conversion into calcium-hydroxyapatite (CaHAp) or octacalcium phosphate (OCP) as reported in the literature²¹.

FTIR spectroscopy: The FTIR spectra of dicalcium phosphate dihydrate- % Cu^{2+} and pure dicalcium phosphate dihydrate are displayed in Fig. 4. When the Cu/(Cu+Ca) is less than 25 %, the spectra are similar to that of pure dicalcium phosphate dihydrate. Moreover, the gradual introduction of Cu^{2+} ions generates a slight shift of some peaks toward low frequencies suggesting that the P-O-Cu bond is weaker than P-O-Ca. This result confirms that the $\text{Cu}^{2+}/\text{Ca}^{2+}$ exchange occurred corroborating the XRD conclusions. The spectra show a broad absorption band between $3600\text{--}2000\text{ cm}^{-1}$, which is assigned to O-H stretching vibrations of $[\text{HPO}_4]^{2-}$ and H_2O . The peak appearing at 1650 cm^{-1} is also attributed to bending vibrations of water molecules. The characteristic bands of $[\text{PO}_4]^{3-}$ are located between $1220\text{--}950\text{ cm}^{-1}$ and those of $[\text{HPO}_4]^{2-}$ at $900\text{--}700\text{ cm}^{-1}$. The bending vibrations of O-P-O bond appear at frequencies below 600 cm^{-1} ^{22,23}. However, the IR spectra of the phases containing copper ions more than 25 %, show the change of the shape bands. The bands assigned to $[\text{HPO}_4]^{2-}$ species becoming weaker and disappear at 60 % of copper ions. There is also displacement of the O-P-O bands to high frequencies indicating the presence of a second phase that can be attributed to dominance of $\text{Cu}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ in the samples.

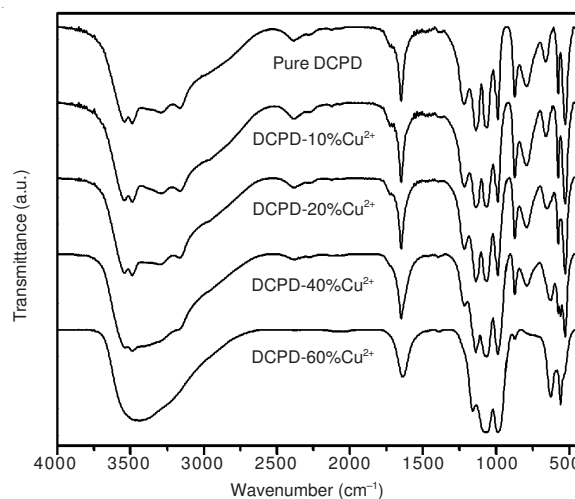
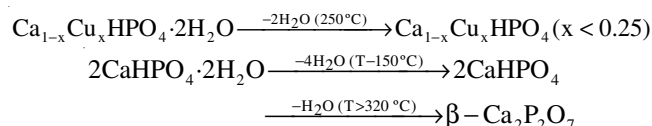


Fig. 4. IR spectra of pure dicalcium phosphate dihydrate and dicalcium phosphate dihydrate- % Cu^{2+}

For the $\text{Ca}_{1-x}\text{Cu}_x\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ samples calcined in air at 250°C , the FTIR spectra (Fig. 5) show that it leads to dehydrated $\text{Ca}_{1-x}\text{Cu}_x\text{HPO}_4$ (DCPA- % Cu^{2+}) with monetite structure, already obtained by direct reaction by Da Silva Filho *et al.*²⁴. When the copper content is greater than 25 %, an additional band appears at 750 cm^{-1} . It is attributed to the vibrations of the P-O-P bond of copper pyrophosphate, in agreement with the previous XRD results²⁵. The reaction involves certainly the following step:



The appearance of pyrophosphate results from the thermal decomposition reaction of the copper orthophosphate which could start at low temperature²⁶.

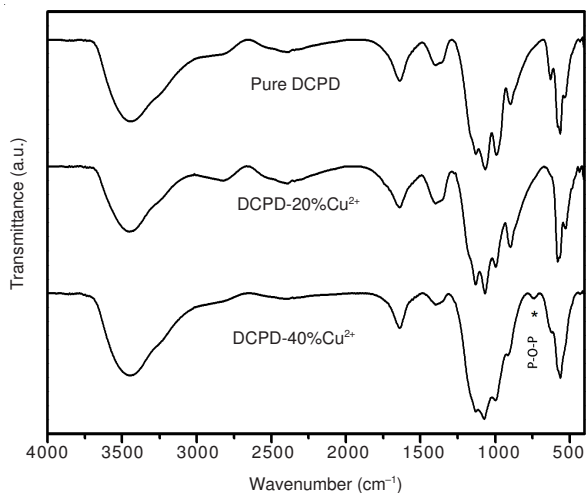


Fig. 5. IR spectra of pure dicalcium phosphate dihydrate and dicalcium phosphate dihydrate- % Cu²⁺ calcined at 250 °C

UV-Visible spectroscopy: The diffuse reflectance spectra of pure dicalcium phosphate dihydrate and dicalcium phosphate dihydrate with different concentrations of copper (10, 20 and 30 %) are displayed in Fig. 6. In the high frequency region, there is a narrow and strong absorption band with a maximum centred near 280 nm (35714 cm⁻¹). Its intensity increases with the increase of copper concentration in the dicalcium phosphate dihydrate. At the same time, the position of the maximum of the peak shifts towards 245 nm. It is mainly due to the O²⁻ → Cu²⁺ electronic charge transfer which progressively substitutes the O²⁻ → Ca²⁺ in the phosphate free of copper. The intensity of the broad absorption band appearing in the visible and near IR regions between 1400-500 nm increases with the increase of the amount of copper incorporated in dicalcium phosphate dihydrate. It is attributed to d-d transitions of Cu²⁺ ions (3d⁹) located in distorted octahedral sites^{27,28}. In fact according to the literature, similar d-d transition band was observed in many copper mixed oxides or phosphates suggesting that the paramagnetic ion Cu²⁺ prefers to locate in the low symmetry in both Ca_{1-x}Cu_xHPO₄·2H₂O and Cu₃(PO₄)₂·H₂O compounds²⁹.

SEM analysis: Fig. 7 displays the SEM pictures showing the morphology and texture of pure dicalcium phosphate dihydrate and dicalcium phosphate dihydrate-% Cu²⁺. The micrograph of pure dicalcium phosphate dihydrate shows that its surface is formed by typical homogeneous crystals. The calcium/phosphorus molar ratio determined by chemical microanalysis (EDS) was found to be stoichiometric and equal to 1 (Fig. 7a). The same stoichiometry was found on dicalcium phosphate dihydrate-20 % Cu²⁺ phosphate surface and leads to molar ratio (Cu + Ca)/P molar ratio close to 1 (Fig. 7b). The morphology of crystals begins to scale compared with the matrix-free copper ions. On the other hand, the surface of

dicalcium phosphate dihydrate-30 % Cu²⁺ (Fig. 7c) does not seem to be regular and the crystal size becomes relatively large. It contains an additional poorly crystallized phase in agreement with the previous XRD and elemental analyses results.

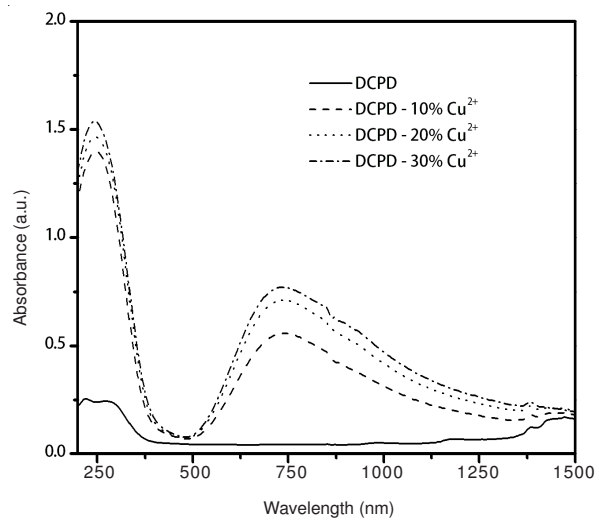


Fig. 6. Diffuse reflectance spectrum of pure dicalcium phosphate dihydrate and dicalcium phosphate dihydrate- % Cu²⁺

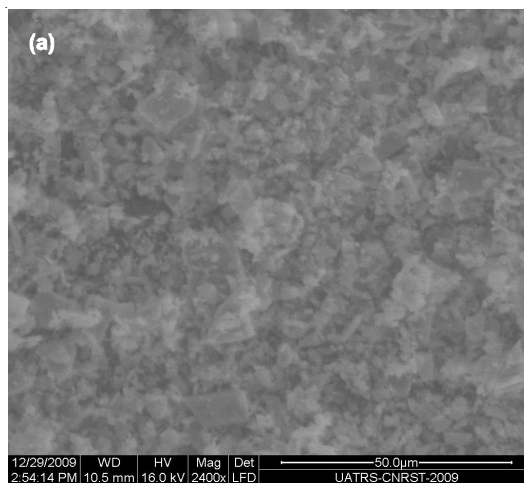


Fig. 7a. SEM image of pure dicalcium phosphate dihydrate

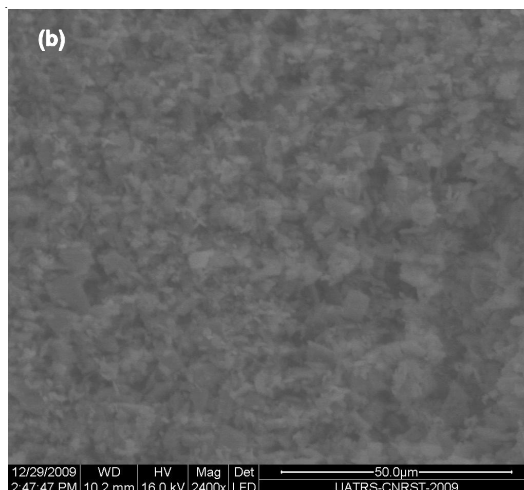


Fig. 7b. SEM image of dicalcium phosphate dihydrate-20 % Cu²⁺

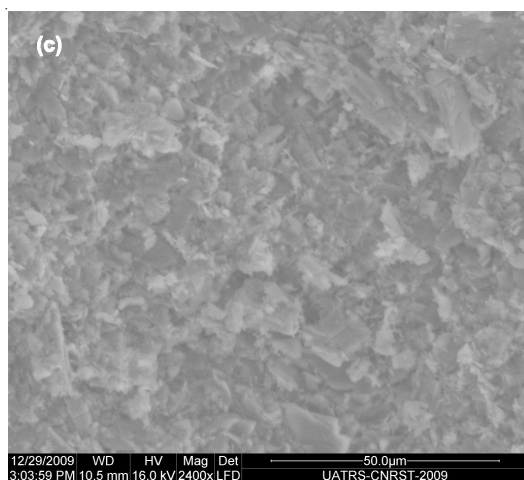
Fig. 7c. SEM image of dicalcium phosphate dihydrate-30 % Cu²⁺Fig. 7. SEM micrographs of pure dicalcium phosphate dihydrate and dicalcium phosphate dihydrate- % Cu²⁺

Table-2 reports the comparison of the elemental analyses with the chemical composition of the surface of the samples, as measured by EDS. It shows that the (Cu+Ca)/P molar ratio determined by elemental analyses are in good agreement with those determined by the EDS surface analysis but much smaller than those applied before the exchange reaction. This decrease of (Cu+Ca)/P is obviously due to the partial substitution of calcium by copper ions which leads to a single solid solution phase. However, in the dicalcium phosphate dihydrate-30 % Cu²⁺ compound, an excess of copper ions is observed and is due to the appearance of the second phase Cu₃(PO₄)₂·2H₂O.

TABLE-2
COMPARISON OF THE CHEMICAL ANALYSES
PERFORMED BY ICP-AES AND EDS

(Cu+Ca)/P molar	DCPD	DCPD-20 % Cu ²⁺	DCPD-30 % Cu ²⁺
Before exchange	1.00	1.30	1.60
ICP-AES analysis	1.01	1.03	1.14
EDS analysis	0.98-1.00	1.00-1.03	1.03-1.30

Conclusion

From the results, the following conclusions can be drawn: The partial substitution of calcium by copper in aqueous media and at room temperature leads to the formation of a new solid solution Ca_{1-x}Cu_xHPO₄·2H₂O, which is isomorphic with pure dicalcium phosphate dihydrate and with solubility limit at 25 % of copper ions. The copper ion accommodate in sites of lower symmetry than those usually chosen by calcium.

In the acidic pH solution, the copper prevents the conversion of dicalcium phosphate dihydrate into products belonging to CaHAp family while, other divalent cations such as Mg²⁺ and Ni²⁺ promote generally this transformation.

For high copper concentrations, another process appears which results from the partial dissolution of dicalcium phosphate dihydrate and its precipitation with copper ions, as already observed when Pb ions are added to apatite CaHAp³⁰.

The calcination of Ca_{1-x}Cu_xHPO₄·2H₂O (x < 0.25) at 250 °C, in air leads to dehydrate materials Ca_{1-x}Cu_xHPO₄ (DCPA) with monetite structure. This method constitutes new way to prepare phosphate monetite at low temperature.

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