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Der Pharma Chemica, 2014, 6(6):133-138
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Preparation of oxygenated apatite from hydrolysis of cured brushite cement in aqueous medium

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ABSTRACT

Several approaches have been developed for the preparation of calcium phosphate cements, some of them are commercially available, and they have proved very effective bone substitutes in different applications. Some of their properties, such as the ability to incorporate different molecules make them very interesting candidates as drug carriers. We were interested in this paper to the study of the hydrolysis after curing a cement composed of the tricalcium phosphate (□-TCP) and monocalcium phosphate monohydrate (MCPM), in aqueous solution with a controlled pH, leading system to transform towards other calcium phosphates known by their very wide including biological and medical applications. In this study the operating conditions are chosen in order to have apatite containing molecular oxygen. Characterization by analyzes (IR, XRD etc.) show that the proposed process provides better results for oxygenated apatite containing together molecular oxygen and peroxide ions. These are removed by heating the final product at a temperature of 300 ° C.

Keywords*:* tricalcium phosphate, monocalcium phosphate, cement, brushite, hydrolysis, oxygenated apatite, biomaterial.

INTRODUCTION

The calcium phosphate cements (CPC) have been discovered and studied first by Brown and Chow [1], and LeGeros et al. [2]. Products cements of calcium phosphate were subsequently operated in the medical field, particularly in the treatment of fractures and for the treatment of maxillofacial deformities [3, 4, and 5]. Since then, new cement formulations have been developed [Mejdoubi [6]; Lemaitre [9-10]; Driessens [11]; Bohner [12-13] to respond specific requirements for other applications, such as fixing metal implants in bone weakened [14,15], vertebral fractures [16-18] and the strengthening of osteoporotic bone [19- 22].

Calcium phosphate cements are distinguished in their applications as compared to other biomaterials, their excellent biological activity by their ability to form a direct bond with the bone and their osteoconductivity. Furthermore, they can be resorbable with a resorption rate which depends on the composition and characteristics of microstructures. After mixing with a liquid phase, the cements (CPC) form a viscous malleable paste, which in some cases may be directly injected during surgery in the bone [23-26].

Currently, many studies have been devoted to the development of the synthesis and study of the association of intrinsic bone regeneration potential of cements (CPC) with their ability to incorporate drugs or other active molecules which are designed to many therapeutic purposes [27-29].

Many studies investigate the oxygenated apatite powders by hydrolysis in aqueous solutions [30-36]. Phosphocalcic oxygenated apatites have showing potential applications in biomaterials because of there antiseptic properties which make them able of limiting the proliferation of micro-organisms at the site of implantation [30]. Recently, composite materials based on calcium phosphate have attracted much attention [37]. Hydroxyapatite is often used as a bone implant material. Lately, the higher attraction of HAp towards protein has been utilized for binding and releasing the active biological molecules [38], was used in the bone cement.

The aim of this work is to study the hydrolysis in an aqueous medium with cured brushite cement synthesized from tricalcium phosphate and monocalcium phosphate. Hydrolysis leads to the cured cement apatitic phase which can incorporate into these tunnels bioactive chemical entities. According to several parameters such as the size and operating conditions, these entities initially introduced into the reaction medium, are inserted in the tunnel apatitic or simply adsorbed to the surface, these products are called oxygenated apatite.

MATERIALS AND METHODS

This method of synthesis consists in reacting promptly two solids as powders, in the presence of an aqueous phase. The solid phase is composed of 10 g of beta-tricalcium phosphate and 8.13 g of monocalcium phosphate. Both products are carefully milled for 30 minutes. The liquid phase is prepared by dilution of 6 g of sodium glycerophosphate ($C_3H_7Na_2O_6P$) in 10 ml of decarbonated distilled water. The cement paste is prepared by mixing the cement powder with the aqueous solution of sodium glycerophosphate on a glass plate for 30 seconds. As a result, the system hardens and takes the form of a non-dry paste. He cement paste before curing is poured into molds to produce cylindrical samples with a diameter of 1 mm and a length of 2 mm. After curing, the samples were removed from the molds and incubated at 50 ° C for 24 hours.

RESULTS AND DISCUSSION

After mixing tricalcium phosphate with monocalcium phosphate reacts according to the following reaction:

$Ca_3 (PO4)_2 + Ca (H_2PO)_2 .H2O + 7H_2O \longrightarrow 4CaHPO_4. 2H_2O$

After mixing, there is an instantaneous formation of brushite, that is shown in the spectrum of Figure 1, by the presence of bands corresponding to brushite (1210.7 cm^{-1} ; 1156.4 cm^{-1} ; 1064.6 cm^{-1} ; 1002.2 cm^{-1} ; 936.6 cm^{-1} ; 725 cm^{-1} ; 613.4 cm^{-1} ; 565.9 cm^{-1} ; 526.1 cm^{-1} ; 494.4 cm^{-1}).

After demoulding the cured parts cement, they are steamed and weighed in an amount of 2 g. We proceed subsequently to hydrolysis of the parts in a solution of 110 volumes hydrogen peroxide, diluted with distilled water and decarbonated, 20% by volume water. We chose two different pH values : 10 and 11. At these pH values the apatite structures are more stable and their formation kinetics is faster. Solid samples of cement are taken, and then promptly dried to stop the evolution of the product.

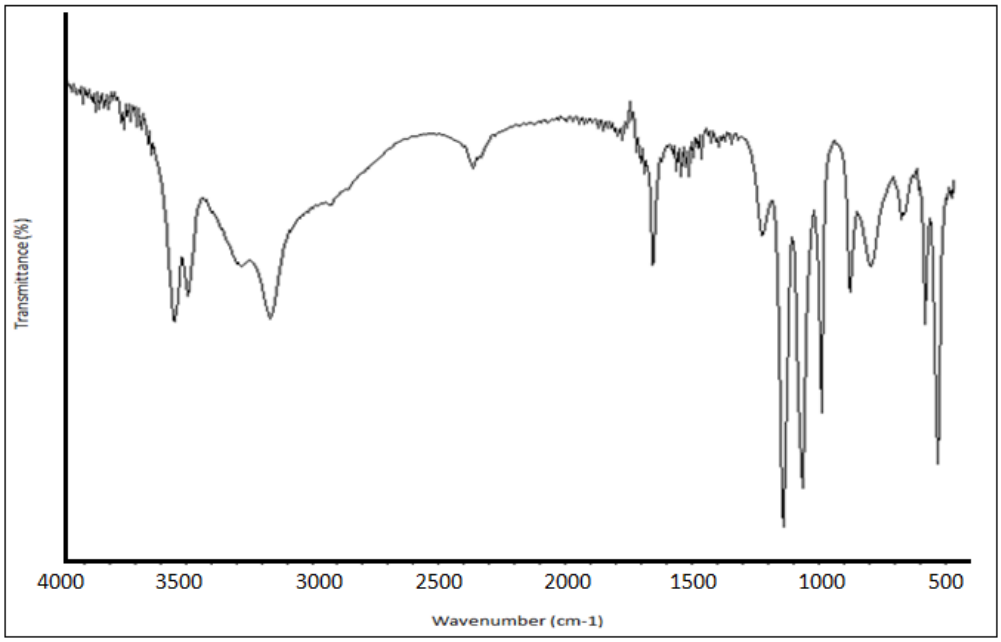

Figure 1. Infrared spectrum of the cured cement

Figures 2 and 3 compare the infrared spectra obtained under the same conditions of pH and at different times.

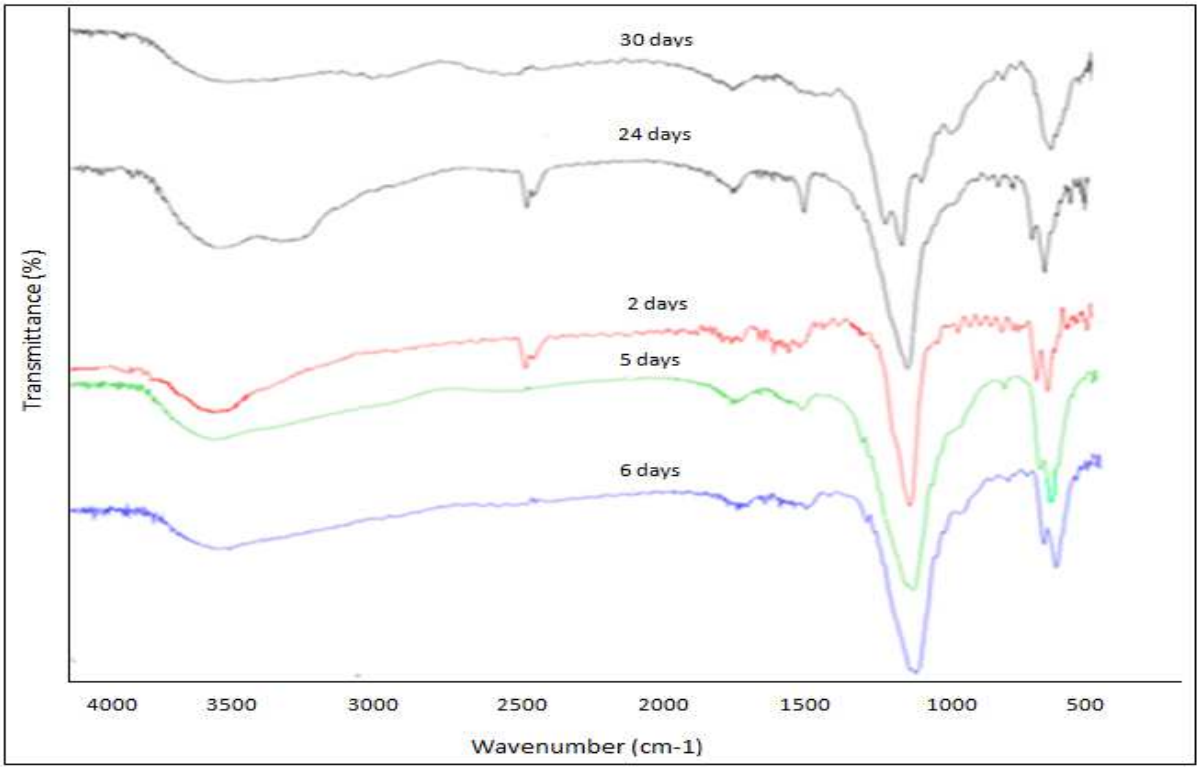

Figure 2. IR spectra of the cured cement evolution, in a solution of H_2O_2 at pH =10

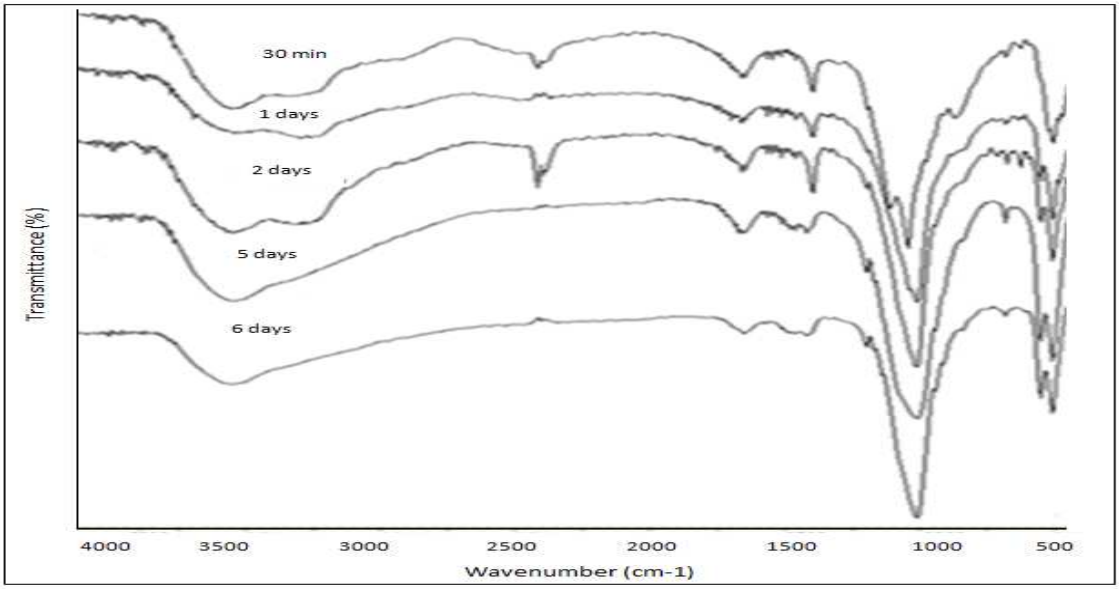

Figure 3. Infrared spectra of the evolution of the cement hardened in a solution of H_2O_2 at pH = 11

Comparing the evolution of the infrared absorption spectra of the cement used in the H_2O_2 solution at pH = 10, shows the evolution of brushite with time to a poorly crystallized apatite structure and slightly carbonated. The latter is formed by the third day. These bands correspond to the structure are present, including bands PO_4^{3-} symmetric vibration absorbent 1043.8 cm^{-1}, 1090.5 cm^{-1} and 962.2 cm^{-1}, and the antisymmetric elongations strips and 601.6 cm^{-1} and 568.7cm^{-1}. It is also noted the appearance of vibration bands and elongation carbonates CO_3^{2-} ions adsorbed on the surface of the apatite. We also observed the absorption bands of OH^- 631.9 cm^{-1} and 3572.0 cm^{-1}. The bands observed at 1632.4 cm^{-1} and 3432.4 cm^{-1} correspond to the water. After 24 hours, the formation of the apatite is not complete, since some bands corresponding to brushite are still present, such as 3541 cm^{-1}, 3489 $cm^{-1}$and 2384 cm^{-1}. Apatite is completely formed after 5 days. All the characteristic bands are present. Over and above the pH = 10, only

a slight influence on the formation of the apatite phase. However uncontrolled product in stock solution a long period causes fluctuations in pH, which promotes the formation of other phosphates instead of apatite.

Thermal study

To study the effect of temperature on the cement after hydrolysis, it was subjected to different temperatures. Figure 4 shows the evolution of oxygen rate as a function of the temperature.

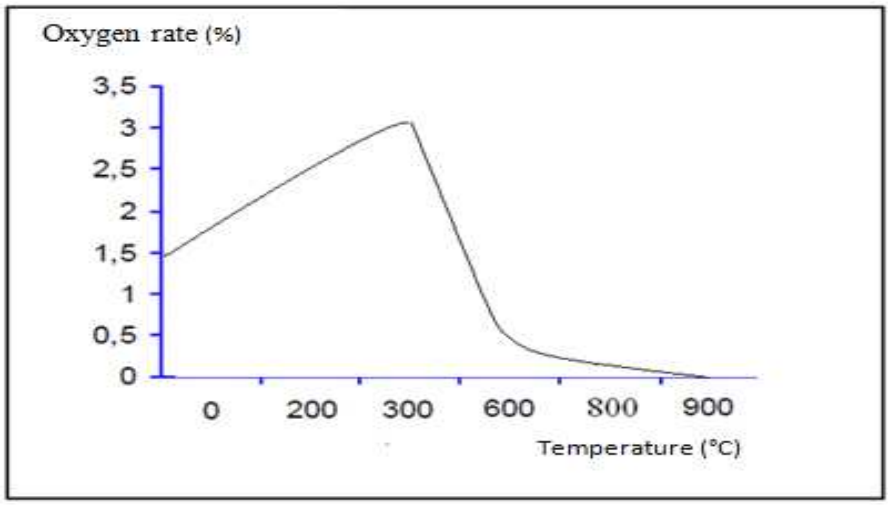

Figure 4. Evolution of the molecular oxygen rates as a function of temperature

Curve 4 shows that the oxygen content increases with temperature up to 300 ° C, and then it starts to decrease gradually to finally disappear at 900 ° C. At 300 ° C, the molecular oxygen content is at maximum; this can be explained by transformation of peroxide ions to molecular oxygen [39]. In fact, after hydrolysis of brushite, it is totally converted into poorly crystallized apatites, which is inserted with oxygen molecules and peroxide ions.

Figure 5 corresponds to the X-ray diffraction of the cured cement after hydrolysis and calcination at 900 ° C. This figure shows that the final phase of the cement is a non-stoichiometric apatite of the fact that it decomposes at 900 ° C at hydroxyapatite and □□□tricalcium phosphate. However, it is deprived of its lime because after calcination, the phenolphthalein test is negative (no pink color).

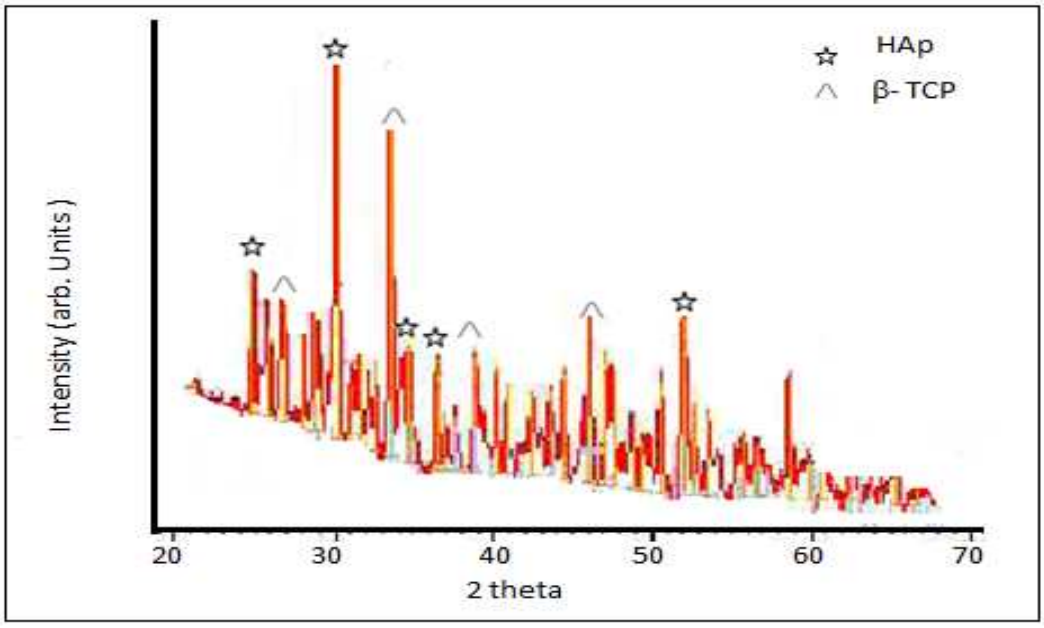

Figure 5. X-ray diffraction of the cured cement after hydrolysis and calcination at 900 ° C

Analysis by transmission microscopy hardened after hydrolysis at pH = 10 cement is presented in Figure 6 shows that the particles have a spherical structure.

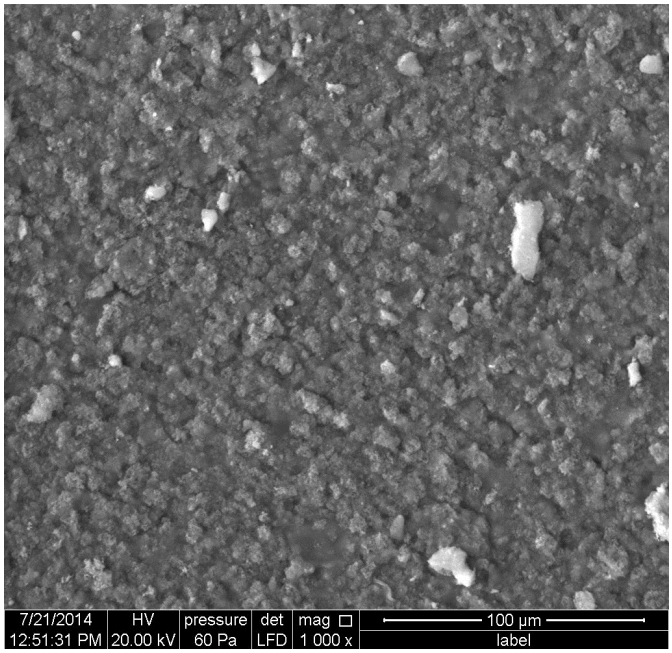

Figure 6. Transmission microscopy of the cured cement after hydrolysis at pH = 10

CONCLUSION

In this work we were able to develop brushite cement and follow its evolution after its dissolution in oxygenated water by varying the pH of the solution

This work has allowed us to make the following remarks:
-The PH of the synthesis is a dominant factor player in the kinetics of chemical reactions of system as proposed Tcp / MCPM, it is the most important factor in the orientation of the chemical evolution of dicalcium phosphate to apatite.
- The basic medium pH = 10 or 11 accelerates the progression system monocalcium phosphate / tricalcium phosphate beta to an apatite. While that below the value 10, the pH of the cement slowed progression. In excess of this value, the effect of pH is almost negative.
- This is probably related to the rate of hydrolysis of dicalcium phosphate, the greater the hydrolysis rate, the faster the oxygen content in the apatite network is higher. Beyond pH = 10, the rate of hydrolysis is insensitive to pH variations. In fact in the presence of dicalcium phosphate, the solution of hydrogen peroxide is becoming more and more deficient in oxygen. The apatite formed in the final stages of hydrolysis is thus less oxygen. The effect of pH can also be explained by the fact that it promotes the deoxygenation of hydrogen peroxide, which makes the low oxygen in the reaction medium when the pH is raised.
- The Analyzes show that the structure of the brushite cement evolves towards a poorly crystallized apatite which contains molecular oxygen and a small quantity of carbonates, coming from carbon dioxide initially present in the solution.

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