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The influence of calcination parameters on free calcium oxide content in natural hydroxyapatite

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Abstract

Effect of calcining temperature and time on the content of free CaO in hydroxyapatite of natural origin is presented. Hydroxyapatite was obtained from pork bones in the course of a three-stage process: hydrolysis with the application of lactic acid, pre-calcination at 600 °C and main calcination stage within the temperature range of 750–950 °C. Calcination was conducted in an electrically heated stationary chamber oven in air atmosphere and in a laboratory scale rotary kiln equipped with a gas burner. The FT-IR spectra confirmed that all organic substances were removed during the calcination process. An increase in free calcium oxide content in hydroxyapatite from 0.003% to 0.023% was caused by the increase of calcining temperature from 750 °C to 950 °C respectively. Calcining time at 950 °C gave a distinct impact upon free CaO content ranging from 0.014% (2 h) to 0.023% (3 h). Hydroxyapatite calcined in the rotary kiln contained the lowest amount of free calcium oxide: 0.002% (750 °C) and 0.003% (950 °C). A method of neutralizing of free calcium oxide, present in calcined hydroxyapatite powders of natural origin, through CaO transformation into hydroxyapatite by application of diluted thermic phosphoric acid has been developed.

Keywords: A. Calcination; Natural hydroxyapatite; CaO; Rotary kiln

1. Introduction

During the last few decades intensive research has been conducted with the aim of producing hydroxyapatite biomaterials of desired biological, physicochemical, and mechanical properties. Biomaterials of animal origin have a structure similar to that of a human bone. In contrast to stoichiometric synthetic apatite, biological mineral contains less hydroxyl groups and a larger amount of carbonate ions [1].

In hydroxyapatite structure the PO_4^{3-} anions may be to some extent substituted with carbonate groups, and this is the so-called type B carbonated hydroxyapatite, as opposed to the A type, where the CO_3^{2-} anions substitute for hydroxyl groups [2,3]. The type A carbonated hydroxyapatite is obtained through the process of high-temperature treatment >1000 °C. In biological hydroxyapatite carbonate anions are also adsorbed on the surface. Substitutions in the anion sub-lattice such as chlorine (0.13 wt%) or fluorine (0.03 wt%) for OH groups are also possible. Calcium ions may be replaced with magnesium (~0.7 wt%), sodium (~0.9 wt%), potassium (0.03%) and a number of trace elements: Sr, Pb, Zn, Cu, Fe [4,5]. The presence of these elements affects the activity of enzymes related to bone cells functioning. The amount of foreign elements incorporated by the substitution depends on the conditions of the structure formation; their presence affects stoichiometry (change in molar ratio of Ca/P), crystallinity as well as thermal and chemical stability reflecting in physical and chemical properties of natural and synthetic apatites [6–8]. The behaviour of hydroxyapatite (HA) at increasing temperature depends on Ca/P stoichiometry and partial pressure of water vapour.

Non-stoichiometric HA decomposes at a lower temperature than the stoichiometric one (even below 1000 °C). As a result of heat treatment tricalcium phosphate $Ca_3(PO_4)_2$ (TCP) as an admixture has been formed, in the ratio of TCP/HA dependent on the Ca/P ratio. The decomposition temperature is also affected by the presence of foreign ions and is usually lower [9,10]. Stoichiometric hydroxyapatite is stable up to a temperature of 1430 °C above which it decomposes into

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α′TCP and tetracalcium phosphate $Ca_4(PO_4)_2O$ (TTCP) [11,12]:

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow Ca_3(PO_4)_2 + Ca_4(PO_4)_2O + H_2O_{(gas)} \quad (1)$$

The temperature at which reaction (1) proceeds increases with water vapour pressure from 1325 °C to 1477 °C [12].

While heating of hydroxyapatite with a higher Ca/P molar ratio (1.67–2.0) αTCP has been forming. It is a stable phase above a temperature of 1340 °C, however, below this temperature it undergoes decomposition resulting in CaO and tetra-calcium phosphate (TTCP) formation. The presence of CaO and TTCP in the mixture with HA, is determined by both the heating and cooling temperature methods [4,11].

Hydroxyapatite with Ca/P ratio close to 1.67 is stable when heated up to a temperature of 1200 °C, and even after a long time of heating at this temperature $Ca_3(PO_4)_2$ is not forming [10,13].

Hydroxyapatite with a ratio of Ca/P = 1.50 heated at 800 °C and 1250 °C transforms completely into $Ca_3(PO_4)_2$. With the increase in molar ratio of Ca/P up to the value of 1.55 the presence of HA, as a distinct phase appears in a mixture with $Ca_3(PO_4)_2$. Powders with the molar ratio of Ca/P within the range of 1.61–1.63 heated at 800 °C contain mainly hydroxyapatite with an additive of $\beta Ca_3(PO_4)_2$. Powders with the molar ratio Ca/P = 1.50–1.62 heated at 1250 °C contain a mixture of low-temperature variety $\beta Ca_3(PO_4)_2$, and a high-temperature variety $\alpha Ca_3(PO_4)_2$. Hydroxyapatite with an additive of CaO is obtained from powders with the molar ratio ≥1.70 after pre-treatment at 800 °C as well as after heating at 1250 °C [4].

Table 1 presents the specification of crystalline phases after calcination concerning the molar ratio of calcium to phosphorus.

Physicochemical properties of synthetic and natural hydroxyapatite vary considerably. The differences arise from both a different molar ratio of Ca/P and the fact that natural HA contains CO_3^{2-} groups and a small amount of foreign elements. It has been established that at elevated temperatures carbonate groups are decomposed. As a result CO_2 has been emitted and free calcium oxide CaO has been formed [4,6,11,12]:

$$Ca_{10}(PO_4)_6(OH)_x(CO_3)_y \rightarrow Ca_{10}(PO_4)_6(OH)_2 + CaO + CO_2 \quad (2)$$

Table 1
Crystalline phases formed as a result of heating calcium phosphates with different molar ratio Ca/P [4].

Molar ratio Ca/P	Crystalline phases forming after heating
1.50–1.67	$Ca_3(PO_4)_2 + Ca_{10}(PO_4)_6(OH)_2$
1.67	$Ca_{10}(PO_4)_6(OH)_2$
1.67–2.00	
$T < 1340$ °C	$Ca_{10}(PO_4)_6(OH)_2 + CaO$
$T > 1340$ °C	$Ca_{10}(PO_4)_6(OH)_2 + Ca_4(PO_4)_2O$
2.00	$Ca_4(PO_4)_2O$

Making hydroxyapatite from animal bones enables to obtain biomaterial with a microstructure resembling that of a human bone with a considerable reduction in the production cost [14,15].

The main constituent of bone is nonstoichiometric hydroxyapatite, containing carbonate ions (CO_3^{2-}) incorporated in bone structure. When bone is pyrolyzed and sintered the carbonate ion undergoes conversion to calcium oxide. As a result hydroxyapatite with an admixture of CaO has been obtained. The presence of CaO in hydroxyapatite ceramics, designed for medical applications, cannot be accepted. In contact with water molecules CaO, if is present in ceramic, converts into calcium hydroxide. That results in gradual tension and hair cracks in the ceramic material, its swelling and breaking and even some disintegration into individual particles and also generates strong alcalinity in the implant environment [16,17].

The problem of the presence of calcium oxide in the HA of animal origin is significant in respect of its applications as biomaterial [18]. For the sake of this problem, we have investigated effect of calcination parameters on free calcium oxide content in hydroxyapatite and elaborated a method of CaO conversion into HA.

The material subjected to calcination temperatures in the range of 600–950 °C at different calcination times was pork bone.

2. Materials and methods

According to the literature organic component can be removed from bone using sodium hydroxide, and then through heat treatment. Methods requiring the application of aggressive factors generate considerable amounts of dangerous wastes which have to be utilized in a special way [19].

Bone material applied in the present work was previously defatted and deproteinized by hydrolysis in lactic acid which guarantees non-agresive conditions and considerable decrease in quantity and quality of generated by-products. There are a few methods of extracting hydroxyapatite from animal bones: thermal decomposition, subcritical water process and alkaline hydrolysis [20–22]. In the research we applied pork bones after acid hydrolysis. The chemical treatment was realised using a mild agent – a solution of lactic acid – and soft conditions: temperature of 125–135 °C and pressure of 0.26–0.30 MPa. As oposed to alkaline hydrolysis, our method eliminates the problem of hazardous alkaline waste management. The hydrolysis process in lactic acid results in bone sludge that can be used for hydroxyapatite extraction and in a protein hydrolysate of high purity used in food industry [23,24].

Thermal analysis was conducted in the air atmosphere by means of SDT 2960 Simultaneous DTA-DTG apparatus produced by the TA Instruments Company. The measurements were taken within the temperature range of 20–1000 °C. The temperature increased at the rate of 20 °C/min. An empty small platinum vessel was applied as a reference sample.

The content of total phosphorus was determined by the differential-photometric method with the use of the UV-VIS

Marcel Media spectrophotometer. The reading of total phosphorus was carried out following the previous mineralization in a mixture of concentrated hydrochloric and nitric acids.

Calcium was determined by titration method using the mixed indicator – calcein and thymolphthalein.

The presence of free calcium oxide in hydroxyapatite ashes was tested by a qualitative analysis of water drains with the application of kalces, a standard indicator showing calcium presence. By applying the ISO standard [23] for hydroxyapatite biomaterials, the presence of free calcium oxide was verified. A water–alcohol phenolphthalein solution was applied for the analyses as an indicator. Hot calcined hydroxyapatite ashes were introduced into water containing a few drops of the indicator.

FT-IR infrared analyses were conducted with the use of Scimitar Series FTS 2000 spectrophotometer produced by the Digilab Company within the basic infrared range of 400–4000 cm^{-1}. The sample of 0.0007 g was pressed with 0.2000 ± 0.0011 g KBr into a pellet. The Deuterated Tri-Glycine Sulfate (DTGS) detector was used for mid-IR range measurements. There were 16 scans, and the resolution was 4.

The AAnalyst 300 Perkin Elmer apparatus conducted with the application of air-acetylene flame and a flame atomizer was applied for the analyses.

The phase composition of the samples was analysed with the use of X-ray diffraction with Philips X'Pert diffractometer equipped with a graphite monochromator PW 1752/00, Cu Kα 1.54 nm, Ni filter (40 kV, 30 mA).

The CaO content was analysed in a water filtrate. 0.8 g of material was introduced into 50 cm^3 redistilled water and that was mixed for 1 h with a magnetic stirrer. Then, the solution was transferred into a flask of the volume of 100 cm^3 and redistilled water was added until the mark level was reached. Afterwards the whole content was filtered through a medium speed filter paper, discarding the first 20–30 cm^3 of the filtrate. The calcium amount was determined with the application of the AAS method and recalculated into free calcium oxide. The multifunction device CX-742 produced by the Elmetron Company was applied in the pH analyses.

3. Experimental part

Seven portions of bone sludge underwent thermal treatment in an electrically heated stationary chamber oven in air atmosphere. The range of thermal treatment temperature of bone sludge calcination was determined on the basis of a preliminary research (Fig. 1).

It can be observed four stages of thermal decomposition of bone sludge. In the first endothermic stage at temperatures up to ~200 °C the desorption of surface water from the sample occurs. This effect, recorded on the TG curve, corresponds to a weight loss of 3.11%. Organic parts decompose in the two following overlapping stages within the temperature range of ~200 °C to ~600 °C. On the basis of protein and fat content analyses, the first weight loss amounting to 13.12% was attributed to the burning of protein, and the smaller second one was attributed to the burning of fat. The last weight loss at a

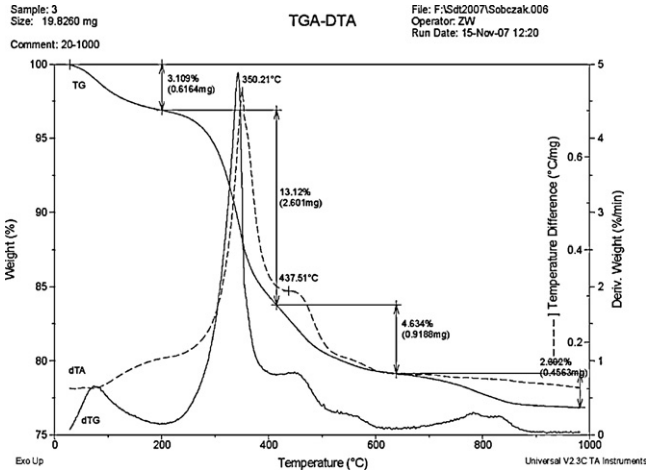

Fig. 1. Thermal analysis of bone sludge.

temperature of ~800 °C is related to the dehydroxylation processes, the thermal decomposition of hydroxyapatite and the loss of carbonate groups present in the natural bone.

Calcination in chamber oven was conducted in two stages. The first stage was at a temperature of 600 °C, while the material was exposed to the maximal temperature for 3 h. In the second stage, the shredded and homogeneous pre-calcined at 600 °C material of the sieve fraction below 63 μm was calcined at three temperatures: 750, 850 and 950 °C, with the application of three exposure times at each temperature: 2, 2.5 and 3 h.

Bone sludge was thermally treated also in a rotary kiln equipped with a gas burner in air atmosphere. The length of the combustion chamber was 1120 mm, and its diameter was 150 mm. All the calcination experiments were conducted with the rotation 0.5 rpm. Bone sludge was introduced concurrently, and the material was added in portions using a tape feeder, with the average feeding rate 100 g of bone sludge per minute. Calcination was conducted in two stages. The first stage was carried out at 600 °C, and then the obtained material was calcined again at temperatures of 750, 850 and 950 °C. The temperature of the rotary kiln output wall was assumed as the calcination temperature.

4. Results and discussion

The colour of material pre-calcined at 600 °C was between dark grey and black because of organic substances, which were not combusted during thermal processing in the rotary and chamber kiln. After second calcination stage at higher temperatures the colour of the materials obtained turned into white as a consequence of carbon removal.

The thermal curves of bone ash obtained at 600 °C are presented in Fig. 2. The total weight loss amounted to 3.67%. In comparison to thermal analysis of bone sludge there were no effects which were attributed to the burning of protein and fat. The other effects were analogous to those at the same temperatures of bone sludge. At temperatures up to ~200 °C an endothermic desorption process of water from the surface of sample occurs. The second weight loss that started at a temperature of ~700 °C is related to the dehydroxylation

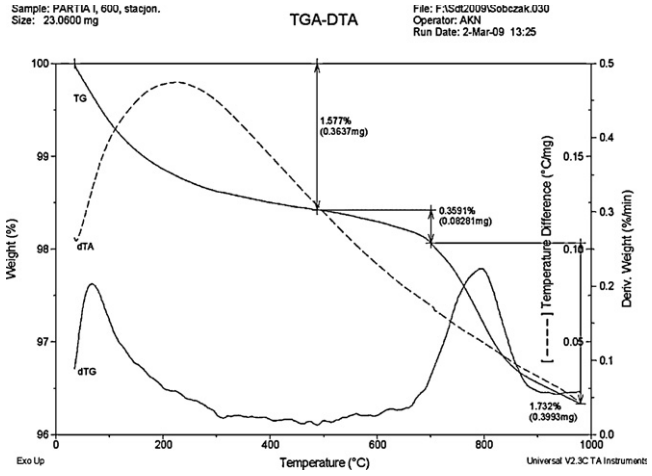

Fig. 2. Thermal decomposition of bone ash after pre-calcination (at 600 °C).

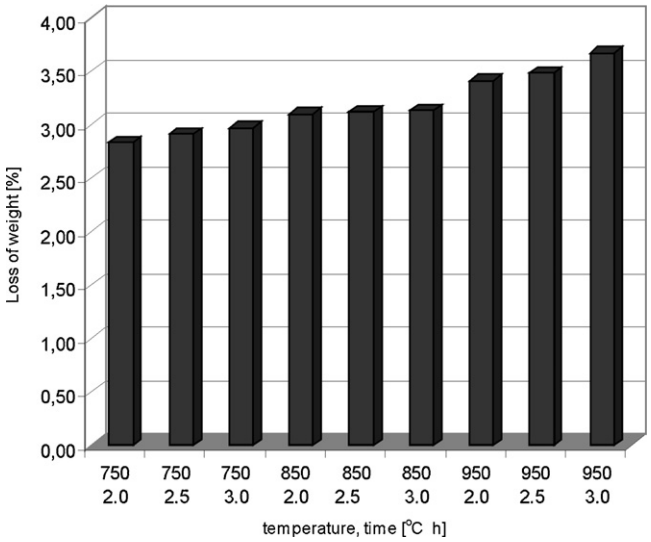

Fig. 3. Weight loss in the second stage of the calcination process.

processes, the decomposition of hydroxyapatite and the loss of carbonate groups.

The measurements of the weight loss obtained in the course of the second stage of calcination are presented in Fig. 3.

Simultaneous increase in calcination temperature and time, increases percentage of weight loss related to burning of organic parts and decomposition of carbonate groups. The weight loss fluctuates between 2.83% for the temperature of 750 °C (2 h) and 3.67% for 950 °C and 3 h. At a temperature of 750 °C the whole organic substance was burnt out. The increase in weight loss is related to the increased dehydroxylation and thermal decomposition of carbonate groups, whose percentage content decreases while time and temperature of calcination increases.

Both phosphorus and calcium content in all the obtained products reaches a similar level of 18.72% for phosphorus and nearly 39% for calcium (Fig. 4). The molar ratio of calcium to phosphorus fluctuates within 1.67–1.75 and this complies with the ISO requirements [23] and qualifies the material for further analyses with regard to biomedical applications. An increased molar ratio of calcium to phosphorus, if compared with stoichiometric hydroxyapatite, may indicate the presence of trace amounts of free calcium oxide. In ashes obtained from bone sludge calcined in the rotary kiln, an increased content of calcium as well as phosphorus was observed while temperature increase was applied. In all the obtained products, the molar ratio Ca/P amounted to 1.68, and was within the ISO standard limits [23]. As far as the products calcined in the rotary kiln are concerned, the calcium and phosphorus content was lower than in the case of the products calcined in the chamber oven. That may be attributed to the shorter calcination time (∼40 min in the rotary kiln) and to the movement of the material inside the combustion chamber.

FT-IR spectra of all the obtained samples is typical of hydroxyapatite (Fig. 5). Bands of the highest intensity within the wavenumbers range 1200–1000 cm^{-1} correspond to the vibrations of the PO_4^{3-} group (asymmetric, stretching). Bands of low intensity within the wavenumbers range 570–560 cm^{-1} correspond to the vibrations of the PO_4^{3-} group (asymmetric). Small bands within the wavenumbers range of 3670–3570 cm^{-1} and within the range of 640–625 cm^{-1} correspond to the stretching vibrations of the OH^- group. An additional

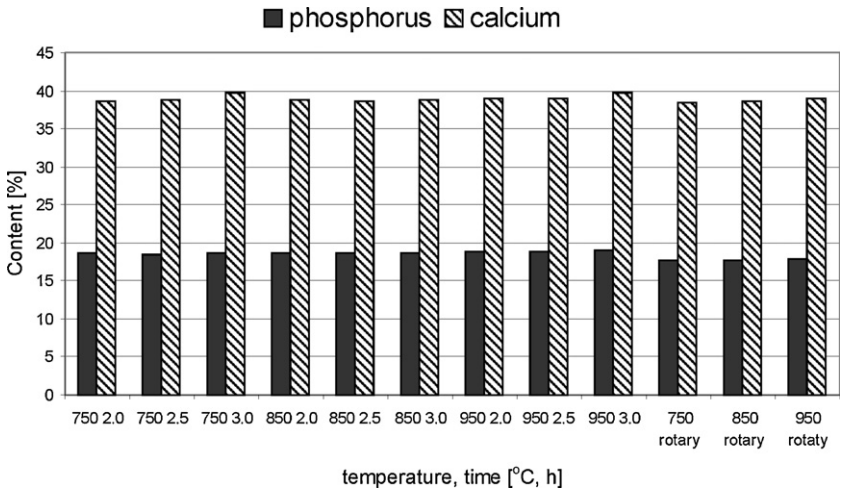

Fig. 4. Calcium and phosphorus content in calcined products.

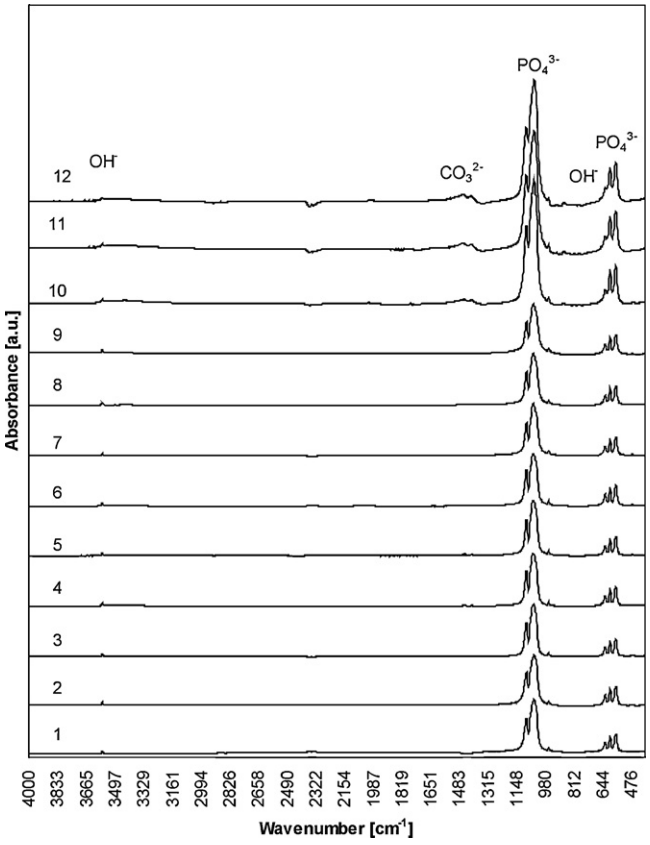

Fig. 5. FT-IR spectra of hydroxyapatite obtained in chamber and rotary kiln Calcination parameters [°C, h]: (1) 750, 2.0; (2) 750, 2.50; (3) 750, 3.0; (4) 850, 2.0; (5) 850, 2.5; (6) 850, 3.0; (7) 950, 2.0; (8) 950, 2.5; (9) 950, 3.0; (10) 750, rotary kiln; (11) 850, rotary kiln; (12) 950, rotary kiln.

weak band corresponding to the vibrations of the CO_3^{2-} groups has been observed in the spectra of the calcined products. The band at 875 cm^{-1} corresponds to the B-type hydroxyapatite, in which carbonate groups are incorporated in places of the PO_4^{3-} anions. The absence of the band at 1550 cm^{-1}, confirms the absence of CO_3^{2-} anions incorporated in place of hydroxyl groups – A-type hydroxyapatite. The presence of polymorphic varieties of calcium carbonate was not established. There are no bands typical of aragonite (713 and 700 cm^{-1}), calcite (712 cm^{-1}) and vaterite (745 cm^{-1}). It was also confirmed that there were no peaks coming from the α and β varieties of calcium pyrophosphate which according to ISO standard [23] may be present together with the wavenumbers 757 and 434 cm^{-1} of the α form, and 1210, 1185, 723 and 454 cm^{-1} of the β form.

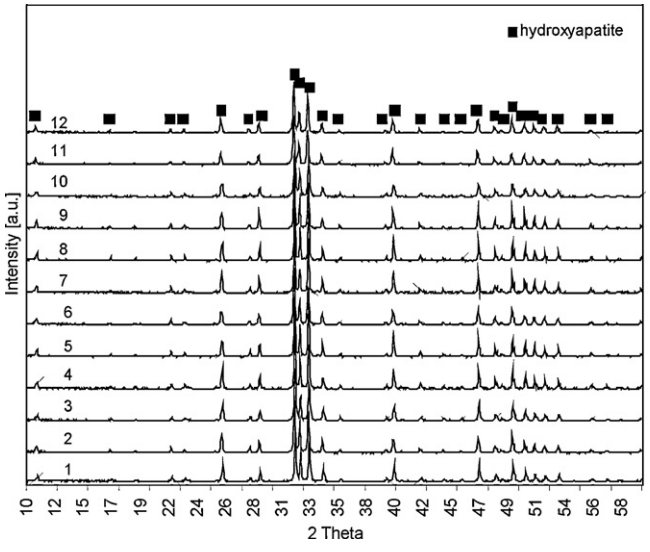

Fig. 6. Diffractograms of calcination products in chamber and rotary kiln Calcination parameters [°C, h]: (1) 750, 2.0; (2) 750, 2.50; (3) 750, 3.0; (4) 850, 2.0; (5) 850, 2.5; (6) 850, 3.0; (7) 950, 2.0; (8) 950, 2.5; (9) 950, 3.0; (10) 750, rotary kiln; (11) 850, rotary kiln; (12) 950, rotary kiln.

X-ray diffractograms of the products calcined in the stationary furnace are presented in Fig. 6. Hydroxyapatite is the only X-ray detectable phase. The temperature and time of the calcination process do not affect the phase composition of the product, however, those parameters influence hydroxyapatite crystallinity. The crystallinity increases with the increase in the calcining temperature and time, which is illustrated by the increased intensity of the peak. On the basis of JCPDS 9-432 the diffractograms obtained contain only peaks of hydroxyapatite. There was no line coming from α ($d = 2.905 \times 10^{-10}$ m) or β ($d = 2.88 \times 10^{-10}$ m) of varieties of tricalcium phosphate (JCPDS 9-348 and JCPDS 09-0169 respectively). $Ca_4(PO_4)_2O$ – TTCP was not found by the standards of JCPDS 25-1137 and JCPDS 70-1379. The calcium oxide was not detected by X-ray diffraction method, (the absence of line $d = 2.405 \times 10^{-10}$ m JCPDS 4-0777). That may be resulted from low amount of CaO – insufficient for the diffractometer to detect.

In order to confirm the presence of free calcium oxide in hydroxyapatite ashes, a qualitative analysis of water drains was performed with the application of kalces. The analyses proved the presence of calcium in water extracts obtained.

The second qualititve analysis was performed using water–alcohol phenolphthalein solution. In all the cases raspberry tint appeared, proving the alkaline reaction.

In order to verify the presence of free calcium oxide, the hydroxyapatite ashes were suspended in water and pH of the solution was measured. Calcium oxide, present in calcined hydroxyapatite, reacts with water molecules forming alkaline calcium hydroxyde.

Fig. 7 illustrates the result of pH measurement depending on the calcination temperature. The pH value of the stoichiometric hydroxyapatite is 8, while bone apatite containing CaO shows

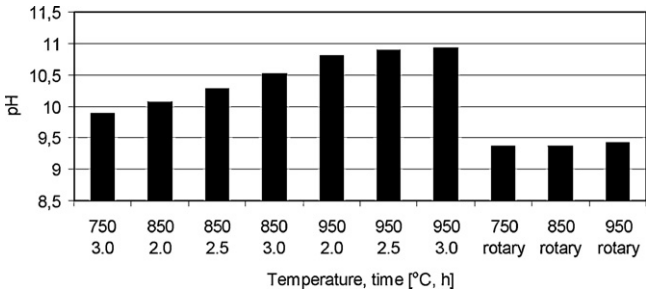

Fig. 7. pH of hydroxyapatite suspensions in water depending on temperature and time of calcination.

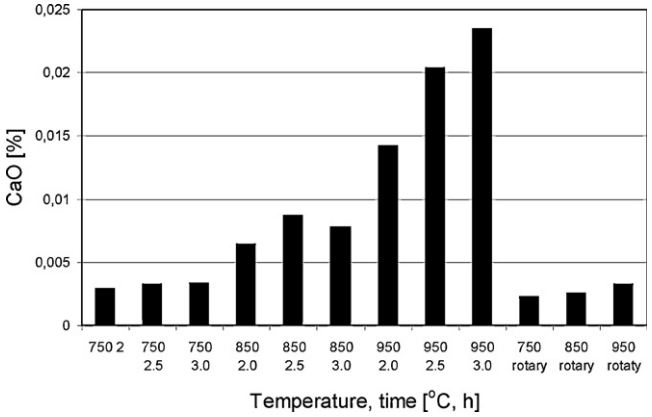

Fig. 8. Calcium oxide content in hydroxyapatite obtained in stationary furnace and rotary kiln.

higher pH. A distinct increase in pH with the increase in temperature and calcination time has been observed.

Analyses concerning the presence of free calcium oxide in calcined products were conducted with the application of the AAS method (Fig. 8). In the case of hydroxyapatite obtained at 750 °C, the observed CaO content was the lowest (0.003%) while in the hydroxyapatite obtained at 950 °C was the highest (0.023%). The above results indicate the significant impact of the calcination temperature on the CaO content in calcined HA.

The results in Fig. 8 have been demonstrated that calcining time influenced the free calcium oxide content in hydroxyapatite. The CaO content increased with increasing calcination time: at 850 °C from 0.006% (2 h) to 0.009% (2.5 h), at 950 °C from 0.014% (2 h) to 0.023% (3 h). The CaO content in material obtained at 750 °C was amounted to 0.003% and was independent on the calcining time. The content of CaO in hydroxyapatite obtained in rotary kiln (Fig. 8) was lower than in HA obtained in chamber oven for corresponding temperatures and amounted to 0.002% (750 °C) and 0.003% (950 °C). Attempts were made to neutralize free calcium oxide present in the calcined products by applying an additive of phosphoric acid at a concentration of 6.24% H_3PO_4. 200 ml of doubly distilled water was added to 50 g of hydroxyapatite obtained in the chamber oven (calcination temperatures: 750, 850 and 950 °C). The mixture obtained was stirred with a magnetic stirrer for 30 min, and then 10 ml of 25% ammonium hydroxide was added in order to maintain pH at a level of 12. Drops of diluted phosphoric acid were instilled into a beaker at the rate of 1 drop per second in a stoichiometric quantity according to the reaction [25]:

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O \quad (3)$$

Reaction was conducted at room temperature. Afterwards the post-reaction mixture was kept for 24 h in order to ensure complete conversion of CaO into hydroxyapatite. The sediment was percolated and washed a few times with redistilled water until pH = 7 was achieved, and then the solid was dried at a temperature of 105 °C and subjected to phase analysis. The phase composition was verified in all the investigated powders, and hydroxyapatite was the unique X-ray detectable phase.

The verification for the presence of free CaO was carried out as described above. The qualitative analysis of the water filtrates was conducted by applying kalces, a standard calcium indicator. The analyses performed confirmed the absence of calcium in water extracts.

5. Conclusions

Effect of calcining temperature and time on a content of free CaO in hydroxyapatite of natural origin has been presented in the paper. Hydroxyapatite was obtained from pork bones in the course of a three-stage process: hydrolysis with the application of lactic acid, pre-calcination at 600 °C and main calcination stage within the temperature range of 750–950 °C. Calcination was conducted in an electrically heated stationary chamber oven in air atmosphere and in a laboratory scale rotary kiln equipped with a gas burner.

(1) *Temperature dependence in chamber oven*. When calcination temperature increases the content of free calcium oxide increases from 0.003% of CaO in hydroxyapatite obtained at 750 °C to 0.23% CaO in obtained at 950 °C.
(2) *Time dependence*. Hydroxyapatite calcined at 750 °C was characterized by the lowest (0.003%) CaO content independent on calcining time (2–3 h).

At higher temperature range (850–950 °C), CaO content was time dependent and increased from 0.006% (2 h) to 0.009% (2.5 h) at 850 °C, and, from 0.014% (2 h) to 0.023% (3 h) at 950 °C.

(3) The content of CaO in hydroxyapatite obtained *in the rotary kiln* was lower than in HA obtained in the chamber oven for corresponding temperatures and amounted to 0.002% (750 °C) and 0.003% (950 °C). The lower CaO content may be related to the shorter calcination time (∼40 min) in the rotary kiln. The influence of the atmosphere inside the rotary kiln, heated non-diaphragmatically with exhausts from natural gas burning, cannot be excluded either.
(4) CaO content in the apatite of natural origin was not detected by the X-ray diffraction analysis presumably due to its small amount. The presence of free calcium oxide in the calcined products was determined by the AAS analysis, which appeared to be the most suitable method for that purpose.
(5) The presence of free CaO, if formed in HA, may be crucial to medical applications. On contact with body fluid CaO can transform into $Ca(OH)_2$ resulting in pH increase and in an increase in implant volume that may lead to its disintegration.
(6) The results obtained have been proved that the admixture of free CaO in HA could be neutralized through its transformation into hydroxyapatite by application of diluted thermic phosphoric acid.

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