DETERMINATION OF PHYSICOCHEMICAL PROPERTIES AND THE THERMAL STABILITY OF HYDROXYAPATITE

OKREŚLENIE WŁAŚCIWOŚCI FIZYKOCHEMICZNYCH I STABILNOŚCI TERMICZNEJ HYDROKSYAPATYTU

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Abstract

Hydroxyapatite [1-3] of structural formula $Ca_{10}(PO)_6(OH)_2$ (HAp) and calcium triphosphate $Ca_3(PO)_2$ (TCP) powder sand suspensions have been characterized physicochemically. Physicochemical characteristics involved the analysis of phase composition using the X ray diffraction, the powder morphology using SEM method, determination of specific surface area by the BET method, the grain distribution of HAp water suspensions using laser diffractometer and the zeta potential as a function of suspension pH (isoelectric point) by the measurement of the electrophoretic mobility.

Key words: calcium triphosphate, polyelectrolytes, slurries, hydroxyapatite

Streszczenie

Badania fizykochemiczne przeprowadzono dla proszków i suspensji hydroksyapatytu [1-3] o wzorze strukturalnym $Ca_{10}(PO)_6(OH)_2$ (oznaczonym dalej jako HAp) oraz trójfosforanu wapnia $Ca_3(PO)_2$ (oznaczonego dalej jako TCP). Badania fizykochemiczne obejmowały analizę składu fazowego przy użyciu dyfrakcji rentgenowskiej, morfologię proszków przy pomocy metody SEM, wyznaczenie powierzchni właściwej metodą BET, rozkład ziarnowy suspensji wodnych HAp przy użyciu dyfraktometru laserowego, oraz potencjału zeta w funkcji pH suspensji (punktu izoelektrycznego) na drodze ruchliwości elektroforetycznej.

Słowa kluczowe: trójfosforan wapnia, polielektrolity, spoiwa, hydroksyapatyt

Introduction

The powders of HAp and TCP were obtained by the wet method [1], they were next dried and then roasted at the temperature of 800°C. Wet methods are based on neutralization of acids and bases, for example $Ca(OH)_2$ and H_3PO_4 or on reactions of calcium salts, for example $CaCl_2$ and $Ca(NO_3)_2$, with phosphates such as Na_2HPO_4, $(NH_4)_2HPO_4$. These reactions occur in aqueous solutions or suspensions. The HAp powders obtained were milled in the attritor with the addition of ethanol, whereas two residual compounds (TCP and HAp + TCP) were milled in the rotating-vibration mill also with addition of ethanol.

Additionally the hydroxyapatite powder was thermally processed in two ways:

- in the first case HAp was roasted for 15 minutes at the temperature of 1200°C,
- in the second case HAp was roasted for 1 h at the temperature of 1200°C.

1. The X ray diffraction and BET measurements

Depending on the kind of original radiation, one deals with X ray, electron or neutron diffraction, if as original radiation are used X rays, electron beam *v*, or neutron beam, respectively.

In the present research the DSH powder method (Debye – Scherrer – Hall method) was applied, which makes it possible to study polycrystalline samples, either powders or solids. In this method the radiation wavelength is constant, whereas the incidence angle is changed. For angles fulfilling the Bragg condition, the reflection on X ray photograph appears (a chart of radiation intensity as a function of angle 2θ).

The determination of powder phase composition was realized on SIEMENS D5005 diffractometer, with angle range of 10 to 70 degrees, using Cu as an anode. The results obtained were compared to catalogue data.

1.1. Specific surface BET measurement

The principle of measurements of the specific surface are consists in the determination of the BET physical adsorption isotherm.

The BET method is based on the adsorption measurement of inert gases such as nitrogen, argon, krypton (used for small values of the determined surfaces) at low temperature (77 K).

The specific surface *S*, that is a surface of 1 gram of adsorbent, is calculated from the formula:

$$S = V_m \cdot N_A \cdot a_m$$

Where:

S – the specific surface area [m²/g]

V_m – the sorption capacity of monolayer for 1 gram of the sample [mol/g]

N_A – the Avogadro number [mol⁻¹]

a_m – the surface occupied by one molecule of gas [m²].

Measurements of the specific surface of selected powders of calcium phosphate were realized using the Autosorb-1 device, according to the constant volume method. The measurement principle is based on the amount of adsorbed gas on the sample surface at a prescribed equilibrium pressure. The application of Autosorb-1 device enabled measurements of the volume of adsorbed and desorbed nitrogen at relative pressures in the range from 0,001 to a 1,0. The adsorption isotherm is determined automatically by a computer program.

1.2. Measurements of particle size distribution and zeta potential of suspensions

The particle size distribution of powders was determined by the light diffraction method (using a LS 13 320 Beckman – Coulter laser diffractometer), enabling the determination of particle sizes distribution in suspensions in the range from 40 nm to 2000 μm. This method gives much better results for polydispersed suspensions (e.g. powders of fire-resistant material) than the dynamic light scattering method.

The zeta potential measurements were performed by the impulse microelectrophoresis using a Zetasizer ZX of Malvern, effectively eliminating the effects of electrolysis (the measuring range of particle sizes from 1 nm to 5 μm, the electrophoretic mobility from 3 nm to 5 μm). The Zetasizer was equipped with an attachment to determine the isoelectric point of suspensions (the zeta potential versus pH relationship) for various ionic strengths.

2. The results of experimental measurements

2.1. The morphology and structure of thermally processed powders

2.1.1. The results of specific surface area measurements

The results of the specific surface measurement of HAp, HAp + TCP and TCP powders obtained by the BET method (5 points) are shown in Table 1.

The HAp powder has the largest specific surface area (30 m²/g), the HAp +TCP

Table 1. The specific surface area obtained by the BET method for HAp, HAp + TCP and TCP powders

Powder	HAp	HAp+TCP	TCP
Specific surface [m²/g]	29,9	14,1	8,4

powder – smaller (14 m^2/g), and the TCP powder has the smallest specific surface (8 m^2/g). The difference between various powders stems from primary grain sizes forming aggregates, whose size equals 60 nm for HAp and 220 nm for TCP.
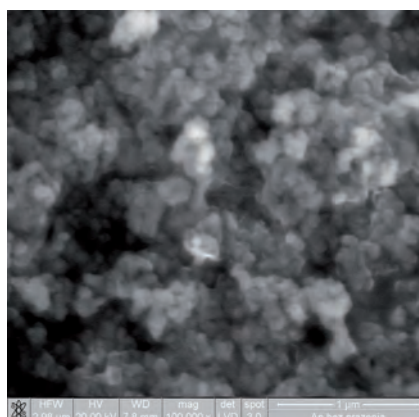
2.1.2. The morphology of HAp powder determined by SM

The morphology of HAp powder was determined using the scanning microscope (Fig. 1) [4].

Apatite
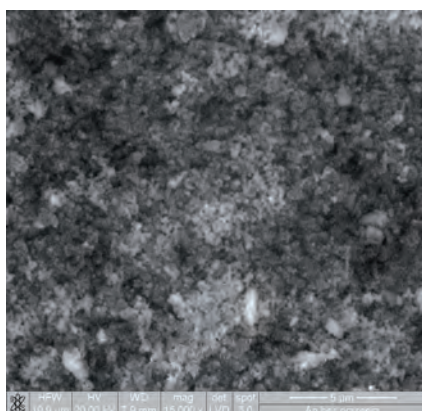
A scanning microscope photograph of apatite powder at a magnification of 15 000

A scanning microscope photograph of apatite powder at a magnification of 100 000

*Fig. 1. The microscope photograph of the apatite scanning microscopy*

The single crystallites and grain aggregates are visible in the pictures of HAp powder. Grains with size of 50 nm have a hexagonal structure characteristic for hydroxyapatite phase.

No significant morphological changes were not observed in samples heated at 1200°C for 15 min whereas in samples heated for 24 h, significant changes in the morphology leading to increase of crystallite sizes achieving 400 nm were observed.

2.1.3. Results of the analysis of phase composition the using the X ray diffraction

The powders roasted at 800°C were analysed. The X ray diffraction has shown that HAp and TCP powders do not exhibit any admixtures which means that the obtained materials are highly phase pure (Figs. 2-3). The presence of hydroxyapatite and whitlockit in the powders of HAp and TCP was stated. The powder roasted at 1200°C were examined in various time periods.

The hydroxyapatite, heated in air at the temperature above 1000°C, loses its water and passes into oxyapatite OCP-$Ca_{10}(PO_4)_6O$.

$$Ca_{10}(PO_4)_6(OH)_2 \xrightarrow{>1000^oC} Ca_{10}(PO_4)_6O + H_2O$$
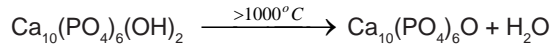
The formation of additional peaks (marked by vertical red line) on the diffractogram at high temperature testifies to the formation of this structure. In the case of short term heating (over 15 min), no significant changes in the HAp structure were not observed.
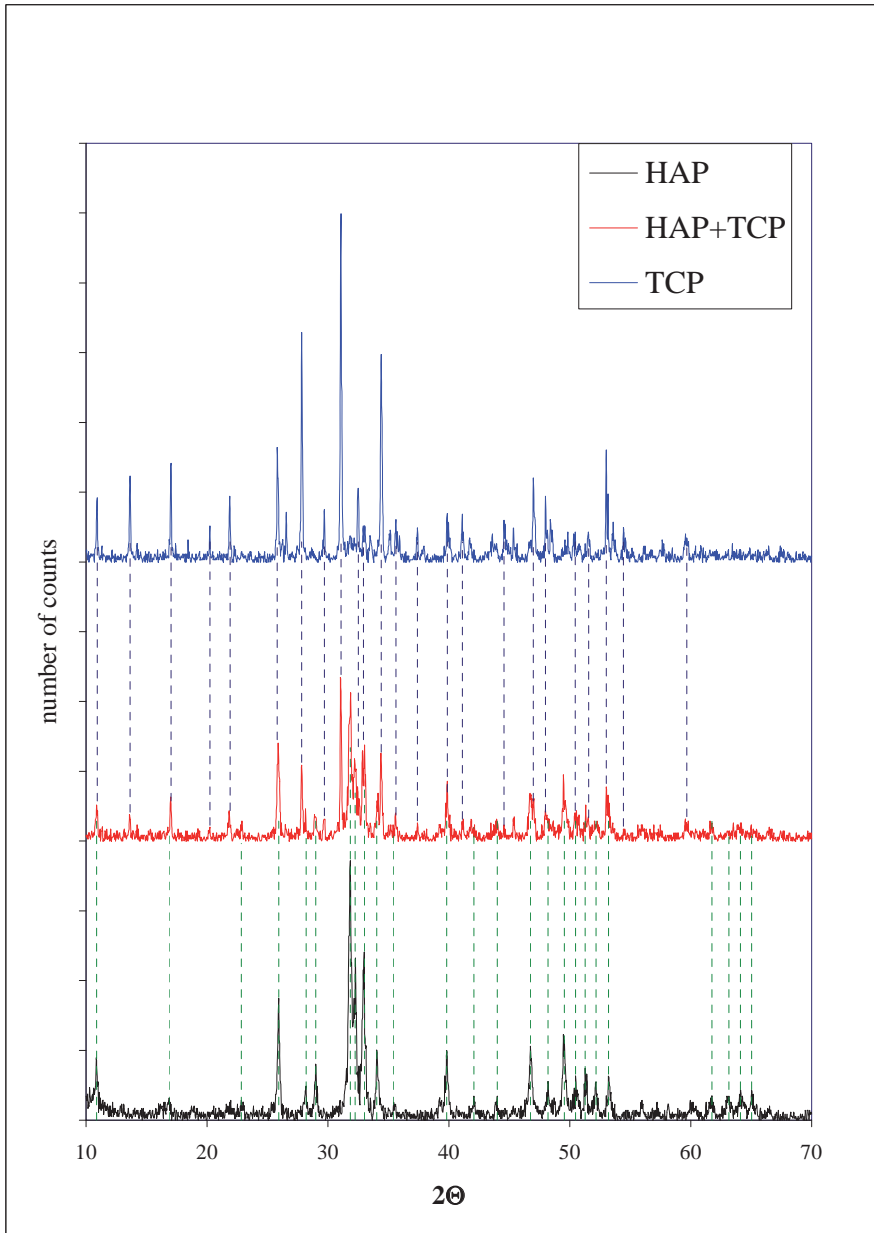

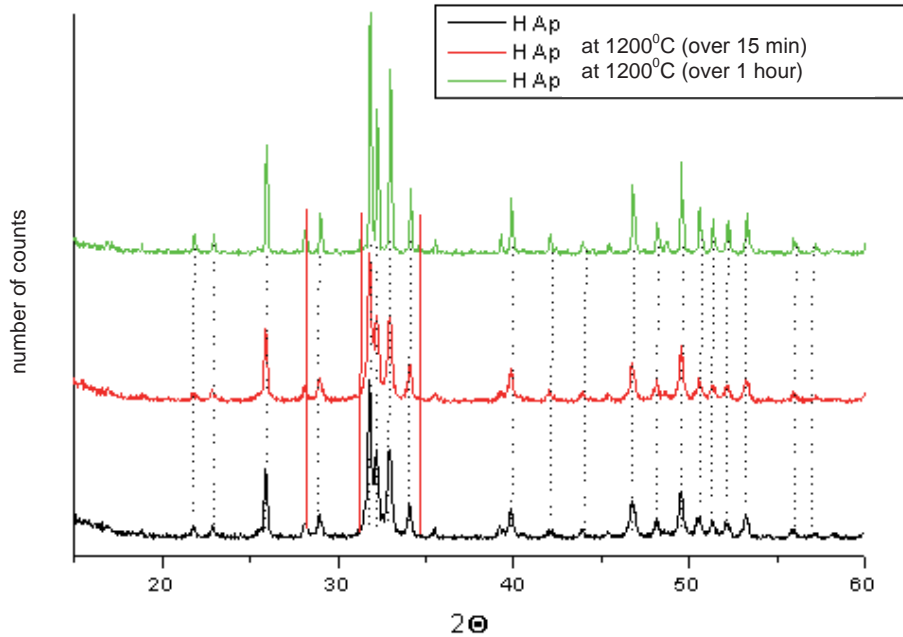*Fig. 2. The diffractograms of the examined HAp, HAp + TCP, TCP powders*

Fig. 3. The diffractometers of the tested HAp powders

2.2. The distribution of particle sizes and zeta potential measurement

2.2.1. The results of particles sizes analysis with application of the laser diffraction method

The results of the grain sizes measurements of powders are shown in the form of histograms in Figs. 4-5.

Basing on the size analysis of the HAp powder (Fig. 4) and the TCP powder (Fig. 5) made by the laser diffraction method it can be stated that each powder is poly-disperse. All studied powders show the presence of small fraction in the range from 50 to 400 nm and medium fraction in the range from 1 to 60 μm. The HAp powder contains also a fraction from 60 to 200 μm.
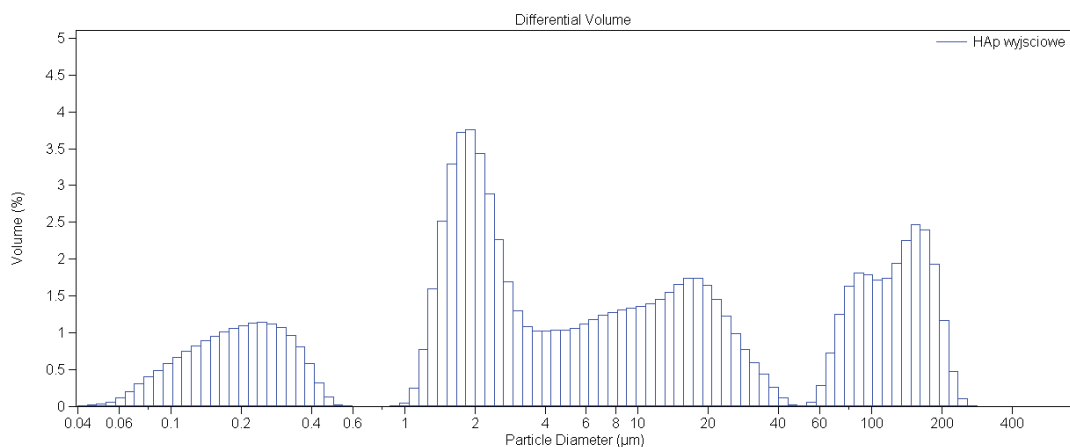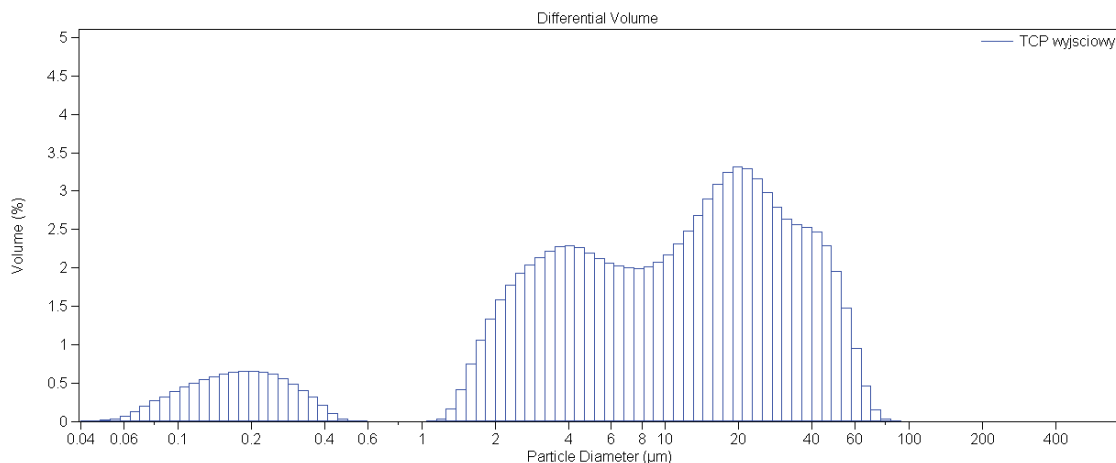
Fig. 4. The distribution of grain sizes of HAp powder

Fig. 5. The distribution of grain sizes of TCP powder

2.2.2 The results of zeta potential measurements

The determination of zeta potential of powders was realized in NaCl of ionic straight equal, 0,001 M and 0,15 M.

In Figs. 6-7 the dependence of zeta potential change of the examined powders on pH is shown. The dependence of zeta potential of calcium phosphate powders on NaCl concentration, changed within the range of 0.001÷0.15 M, was examined.
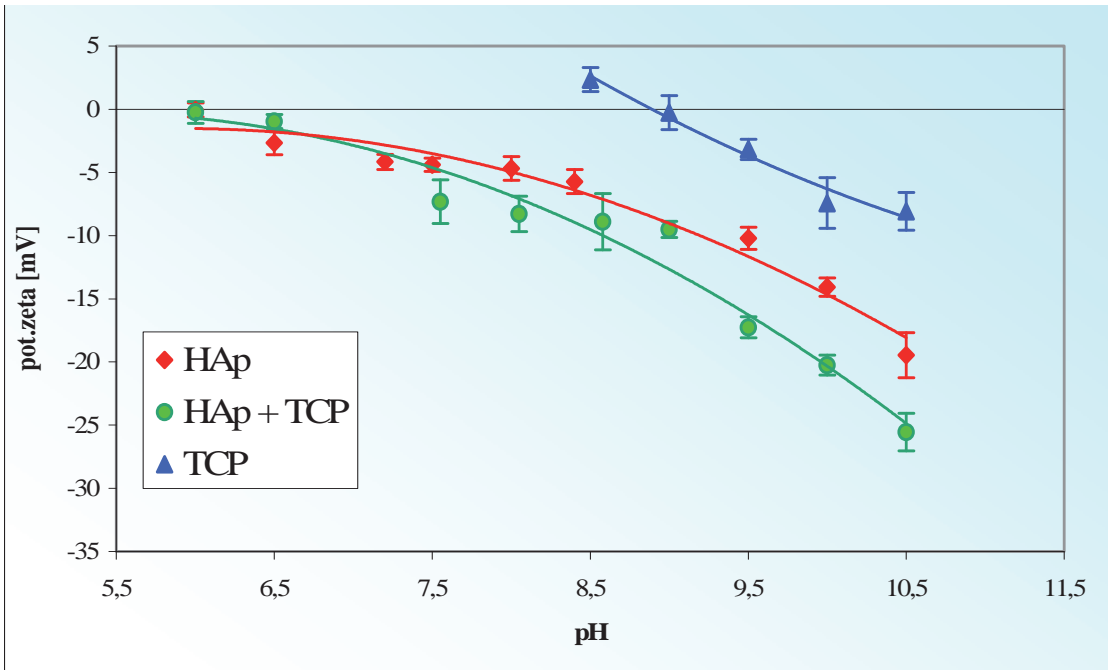
Fig. 6. The change of zeta potential of the examined powders vs pH value of NaCl solution with concentration of 0,001 M.
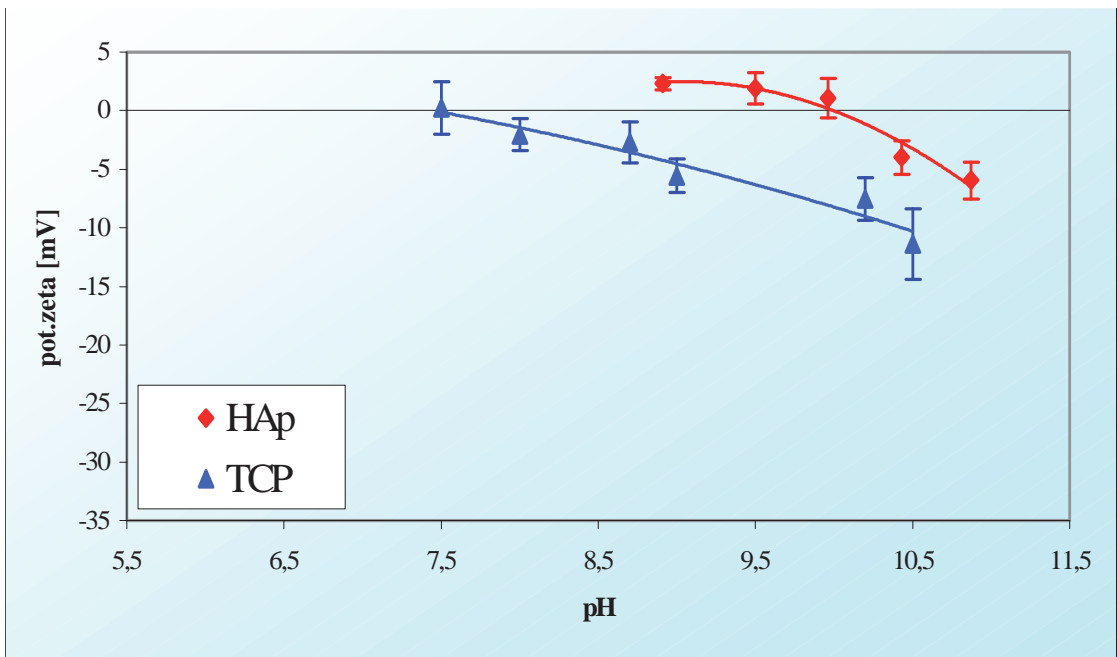

Fig. 7. The change of zeta potential for HAp and TCP powders vs pH value of NaCl solution with concentration of 0,15 M

As can be observed for I = 0.001, the isoelectric point of the TCP appears at pH of 9, while for HAp powder and HAp + TCP powder at pH of 6. With increase of pH, the most negative values of zeta potential correspond to HAp + TCP powders. For two phase powder at pH of 10,5, the zeta potential reaches a value of -25 mV, while for HAp and TCP powders this value is -20mV and -5 mV, respectively.

As can be observed, the isoelectric point of TCP powder occurs at pH of 7,5, while for the HAp powder it exists at pH of 10. The zeta potential of examined powders, with increase of NaCl solution pH with concentration of 0,15 M, does not achieve such negative values as in case of NaCl solution with concentration of 0,001 M. It is the result of the changing ionic strength of the solution. The NaCl solution with concentration 0,15 M has the ionic strength corresponding to the physiological ionic strength.

Conclusions

It been has shown, that polydispersive HAp powder consist of primary grains (crystallites) with sizes of 60 nm. The short-time heating (up to 15 min) at the temperature of $1200^{o}C$ does not cause significant structural and morphological changes of HAp powders.

References

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