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## Research of Reagent Concentration Effect and the Synthesis Temperature on the Physicochemical Characteristics of Nano-Sized Silicon-Containing Hydroxyapatite.

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### ABSTRACT

This paper presents the results of nano-sized silicon-containing hydroxyapatite (Si-HAP) synthesis. Si-HAP samples  $(Ca_{10}(PO_4)_6-x(SiO_4)_x(OH)_{2-x}, 0 \leq x \leq 2)$  were synthesized by the precipitation from solutions. Calcium hydroxide saturated solution, the solution of phosphoric acid (10-40%), tetraethoxysilane were used as the reagents. The influence of various factors on the crystal size and morphology was studied. The radiographic examinations were performed with a diffractometer and by transmission electronic microscopy. The specific surface area was measured by low temperature adsorption and thermal desorption of nitrogen with a gas adsorption analyzer. Synthetic Si-HAP crystals were obtained. The size of such crystals made 2.5 nm and its specific surface area made  $136.7 \text{ m}^2/\text{g}$  at the following synthesis parameters:  $x = 1.5$ , the phosphoric acid concentration made 30% and the temperature was  $20 \text{ }^\circ\text{C}$ .

**Keywords:** nanosized silicon containing hydroxyapatite, synthesis parameters, the size and morphology of the particles, the degree of silicate ions substitution, the specific surface area.

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## INTRODUCTION

The development of biomaterials for damaged bone tissue replacement is a promising quickly developing area of research. Among the various types of synthetic materials used for this purpose, hydroxyapatite (HAP,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) which with some assumptions may be considered as the crystal and chemical analog of the mineral component in the skeletal tissue of animals and humans [1-4]. This material as an implant stimulates the growth of bone cells and the formation of a new bone, but it is slightly soluble in body fluids [2,5]. The materials that contain silicate ions were developed to improve the rate of hydroxyapatite and bone tissue integration [6]. The directed synthesis of silicon-containing apatites is a complex physico-chemical problem. So the study of the synthesis parameters influence on the morphology and physicochemical properties of Si-HAP products plays an important role in the development of biocompatible osteomaterials.

The aim of this work is to study the dependence of the physicochemical properties of the silicon containing modified HAP on the degree of silicate ions, phosphoric acid concentration and temperature synthesis.

## METHODS

Si-HAP samples ( $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x(\text{OH})_{2-x}$ ,  $0 \leq x \leq 2$ ) were synthesized by the precipitation method from solution as described in the article [7]. The saturated calcium hydroxide solution, the solution of phosphoric acid, tetraethoxysilane were used as the reagents. The synthesis was performed using various reagents at different temperatures with certain feed and ingredient mixture rates.

X-ray studies were carried out with a diffractometer Rigaku Ultima IV (Japan) and D / teX Ultra detector. The survey was conducted in reflection mode (Bragg-Brentano geometry) using  $\text{Cu K}_\alpha$  radiation (the wavelength ( $\lambda$ ) = 1.54178 Å). Generator operation parameters: accelerating voltage makes 40 kV, the tube current makes 40 mA. The survey options: angle range makes  $2\theta = 85^\circ \pm 5^\circ$ , the step range makes  $2\theta = 0.02^\circ$ , spectra recording speed makes  $3^\circ/\text{min}$ , the crystal size was determined by Williamson-Hall method based on XRF data.

Electron microscopy morphological examinations of Si-HAP samples as the hydrogel were carried out on a transmission electron microscope JEM 2100 (JEOL Ltd., Japan) with the resolution of 0.2 nm. The accelerating voltage of the electron gun made 200 kV, the cathode material is a single crystal of lanthanum hexaboride ( $\text{LaB}_6$ ), the leakage current at the turned on cathode makes 101.5 uA. The images were obtained at the transmission mode and the magnifications up to 40000x. The determination of a specific surface area by the BET method was implemented with an automated sorption device TriStar II 3020 with the use of surround variant. The specific surface area was calculated by the low-temperature nitrogen vapor sorption according to isotherm and the single-point BET method at P/Po point = 0.3189. The samples were incubated by inert nitrogen and helium gas while providing the simultaneous heating of samples at the temperature of 350°C.

Tetraethoxysilane oxide, oxide and phosphoric acid at the concentration of 10, 20, 30 and 40 % were used as the reagents. The synthesis was performed at the temperatures from 22 to 80 ° C with an acid feed rate of 1 ml/min.

## MAIN PART

The amounts of the reagents were determined according to stoichiometric calculations, assuming that the silicate ion substitutes for a phosphate group in a crystal HAP grid crystal at the range of 4%, and the ratio  $\text{Ca}/(\text{P}+\text{Si}) = 1.67$  remains a constant one. To examine the dependence of physical and chemical properties on silicon content Si-HAP samples were prepared at different degrees of of silicate ions substitution ( $x = 0.5, 1.0, 1.5, 2.0$ ) with a flow rate of 10%  $\text{H}_3\text{PO}_4$  solution of 1 ml/min at the room temperature [8]. The results are shown in Table 1.

According to Table 1 the introduction of silicate ions into the crystal HAP grid ( $x = 0.5, 1.0, 1.5$ ) causes a significant reduction of crystal size, which is reflected in the specific surface area (Fig. 1b). The highest

specific surface area has Si<sub>2.0</sub>-HAP (x = 2) 122.22 m<sup>2</sup>/g, which is 4 times higher than an unmodified hydroxyapatite.

**Table 1: Physico-chemical characteristics of Si-HAP samples (n = 3, p = 0.95)**

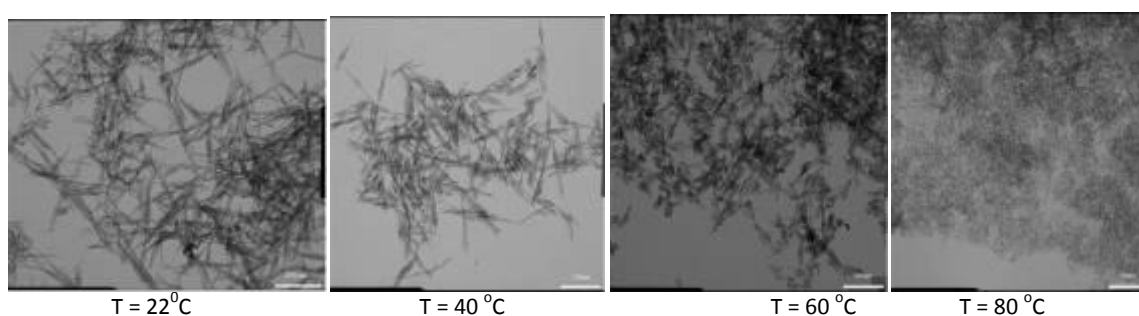
x	Si content in the sample, %	Crystal size, nm	Specific surface area, m <sup>2</sup> /g
0.0	0.00	65.5	27.7
0.5	1.40	19.3	59.1
1.0	2.85	12.8	66.0
1.5	4.31	11.4	108.9
2.0	5.81	11.7	122.2

This regularity is observed by the initial concentration of orthophosphoric acid increase (Table 2). When the initial concentration of H<sub>3</sub>PO<sub>4</sub> 20-40% (by weight) is used Si<sub>1.0</sub>-HAP crystal size is sharply reduced by about 5 times. This is due to the occurrence of a large number of nucleation sites in the reaction zone at high acid concentrations.

**Table 2: Physico-chemical characteristics of Si<sub>1.0</sub>-HAP at different concentrations of orthophosphoric acid (n = 3, p = 0.95)**

Registered parameters	H <sub>3</sub> PO <sub>4</sub> concentration, % by weight.	Crystal size, nm	Specific surface area, m <sup>2</sup> /g
Acid flow rate: 1 ml/min. Substitution degree x= 1.0 Reaction temperature: room temperature Stirring speed: 1200 rev./min	10	12.8	92.0
	20	2.9	128.7
	30	2.5	136.7
	40	2.6	125.2

To study the temperature effect on the particle morphology, Si<sub>1.0</sub>-HAP was synthesized at different temperatures: 22, 40, 60 and 80 °C. The form of Si<sub>1.0</sub>-HAP particles was determined by transmission electron microscopy with an integrated energy dispersive analysis detector on the device Tecnai G2 20F S-TWIN. It is found out that Si<sub>1.0</sub>-HAP particles at low temperature synthesis form needle-shaped crystals, and at high temperature synthesis the obtained clusters of crystals have a small grade form (Fig. 1).



**Figure 1: Reshaping of Si<sub>1.0</sub>-HAP nanoparticles depending on the synthesis temperature**

It is also found that the temperature increase affects the ions mobility and the reaction rate which result in precipitate particle size increase and the specific surface area reduction. (Fig. 2)

Fig. 2 Crystal size (a) and specific surface area (b) Si<sub>1.0</sub>-HAP dependence on synthesis temperature

X-ray phase analysis (XRPA) showed that all the Si-HAP samples synthesized at the temperatures below 60 °C using phosphoric acid in various concentrations, are single phase ones, and the synthesis result observed at 80

° C revealed the presence of  $\text{Ca}(\text{OH})_2$  phase in products, which is related to the calcium hydroxide solubility decrease and its precipitation.

### SUMMARY

The obtained results confirm that the variation of HAP synthesis parameters HAP significantly affects the shape and dimensions of the crystals. This allows, depending on the HAP application, to obtain the samples with prescribed physico-chemical properties. The physico-chemical characteristics of Si-HAP crystals, obtained in this study correspond to the materials used in osteosynthesis: they are able to adsorb actively on the surface of collagen fibers, which provides high biological activity and biologic resorbability of Si-HAP [9,10].

### CONCLUSION

- The substitution of phosphate ions with the silicate ions leads to the crystal size reduction in 5 times compared with the unmodified HAP (65.5 and 12.8 nm, respectively).
- The use of phosphoric acid (30% solution) in the synthesis allows to obtain the crystals of 2.5 nm.
- The synthesis temperature influences the shape and the size of crystals at the temperature of 20 °C. The minimum size of such crystals makes 2.5 nm.
- Optimal synthesis parameters are determined. These parameters allow to obtain a product with the specific surface area of 136.7 m<sup>2</sup>/g.

The studies were performed using the equipment of the collective use Centre of "BelSU" SRI

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