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Features of crystallisation in system $Ca(NO_3)_2–(NH_4)_2HPO_4–NH_4OH–H_2O$

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For today considerable progress will reach at use of biologically active materials on the basis of the substances initially close on chemical and phase structure to a bone fabric, – calcium orthophosphates [*Veresov,* 2004, *Ezhova*, 2000].

Phosphates of calcium widespread in the nature. They meet in the form of minerals, such as apatites, брушит, etc., and also are important building components of firm fabrics of the person. Synthetic analogues of biogene minerals possess property of biocompatibility, therefore studying of crystallisation of phosphates of calcium, in particular hydroxyapatite, in various conditions *Kibalchits V. L, V. F.Komarov*, 2000 gives the chance in the long term workings out of materials and composites with the set properties for fabric engineering and orthopedy [*Barinov., Komlev*, 2005, *Danilchenko*, 2007].

The purpose of the given work - research of influence of acidity of environment on phase education in system Ca $(NO_3)_2–(NH_4)$ $_2HPO_4–H_2O$. Following problems were thus solved: 1) to receive a series of samples hydroxyapatite at a variation pH the reactionary environment and 2) to study influence pH on phase structure of deposits, crystallinity, morphology, solubility and some other characteristics.

During experiments sedimentation hydroxyapatite spent by slow draining of solutions of nitrate of calcium and disubstituted phosphate of the ammonium, taken in the ratio $n_{\text{starting}} = Ca/HPO_4 = 1.70/1$. pH the received solution corrected to a preset value from an interval from 4.00 till (solutions HNO_3 (1:1) or NaOH (20 %)). The received deposit analyzed Ik-spectroscopy methods, Rentgeno-phase analysis , optical microscopy. In supernatant liquids methods of the chemical analysis defined residual concentration of phosphates-ions and calcium ions. pH systems defined size potentiometric.

Under the received data it is established that deposit formation in studied system is observed at pH ≥ 5.50. In these conditions, it agree to data Rentgeno-phase analysis (fig. 1) and IK-spectroscopy, there is a sedimentation brushite $CaHPO_4{\cdot}2H_2O$ (fig. 2).

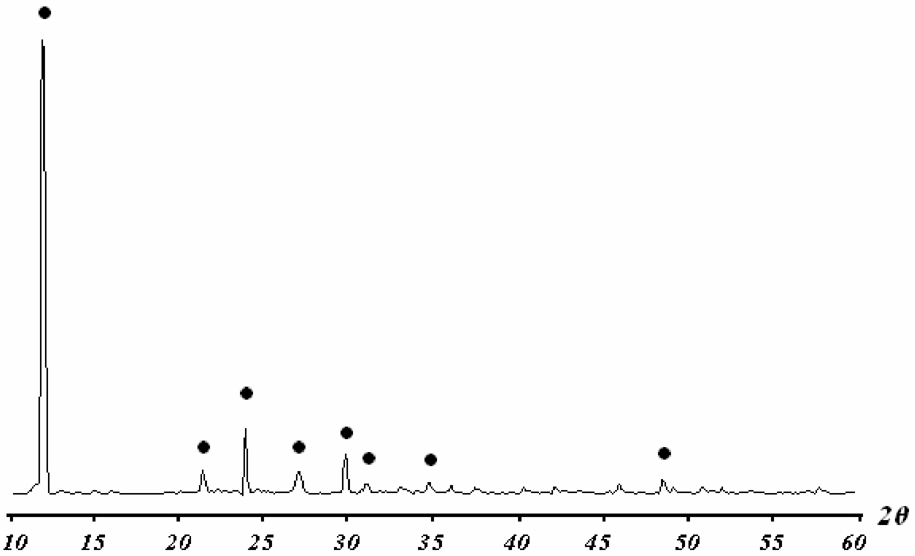


Fig. 1. Difraktogram of the sample received at pH=5.50

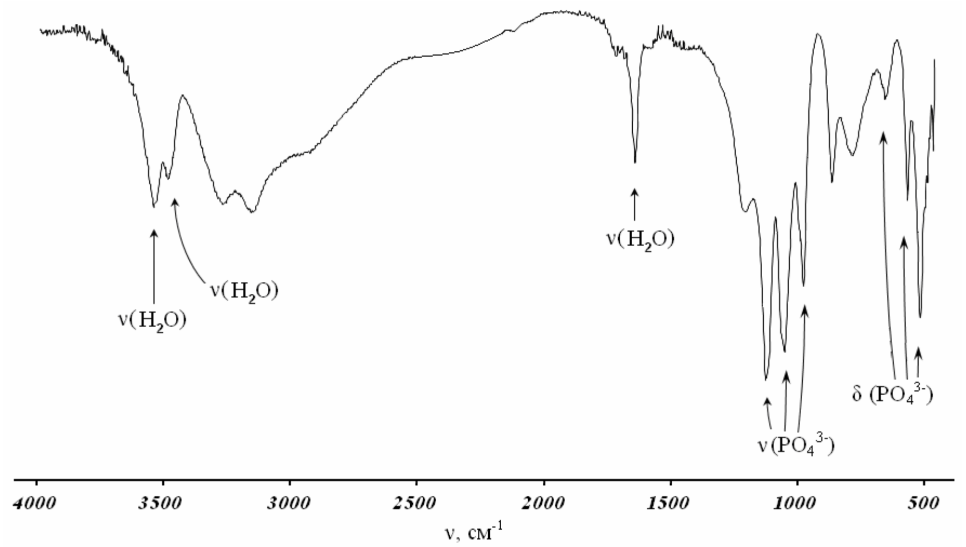
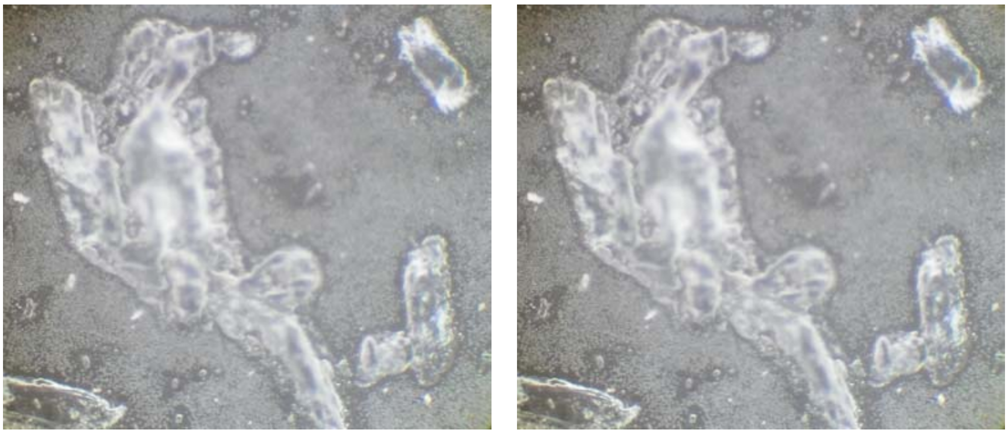


Fig. 2. IK-spectrum of the sample received at pH=5.50

Research of morphology of particles of a firm phase has shown that after updating of acidity of environment to value 5.50 ± 0.05 in a solution drop on subject glass the thin extended accurately not generated plates brushite (fig. 3a) crystallise. After two days of maturing of substance in a uterine solution, more accurate faceted crystals of two-water hydrophosphate of calcium (fig. 3b) which remain after drying of a mineral phase are formed.



a b

Fig. 3. Photos of samples from solutions: a - pH=5.50,b - pH=6.00

At value increase pH it is possible to track change of morphology of crystals. At the first stage of crystallisation after draining of reagents and updating pH in the drop selected from system are formed small diamond-shaped transparent кристаллики brushite which in process of maturing grow in a solution and partially turn to less soluble phase – hydroxyapatite. In the dried up deposit also it is observable joint presence of lamellar crystals brushite and hydroxyapatite in the form of units of the smallest crystalline particles of the various form.

By results of РФА the firm phases received during experiment at pH > 7.00, are presented only hydroxyapatite. And improvement of the permission of peaks in the field of 30–35 bragg reflexion corners on difractogram synthetic samples hydroxyapatite, and accordingly and increase of their degree of crystallinity at growth pH synthesis from 7.00 till (fig. 4) is observed.

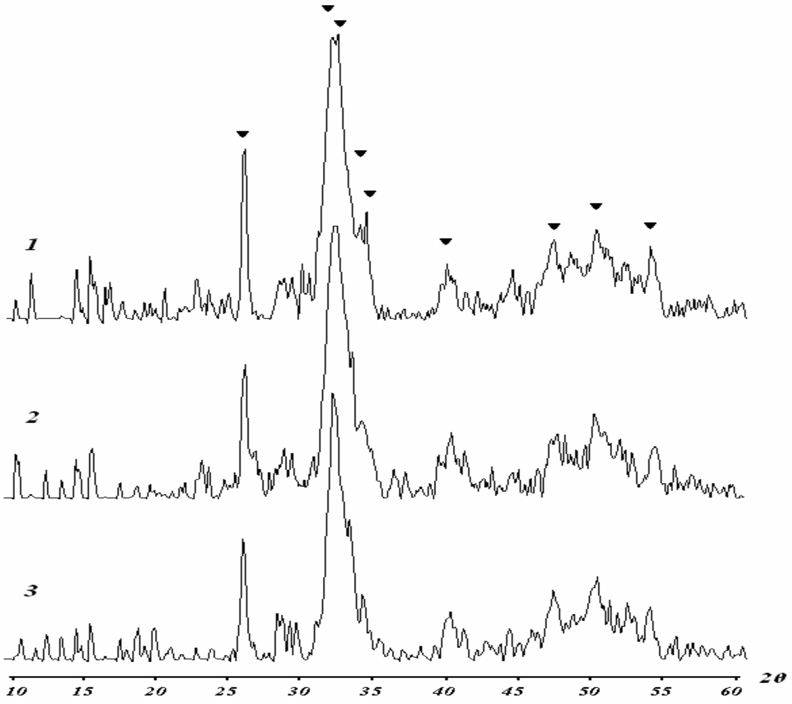


Fig. 4. Difraktograms of samples of the deposit received at various values pH:
1 – pH=6.50, 2 – pH=7.00, 3 – pH=11.00 (a phase - hydroxyapatite)

According to Rentgeno-phase analysis by means of the formula of Seljakova-Sherrera the sizes of crystalline particles (tab. 1) are calculated.

Table 1. Dependence of the sizes of crystalline particles hydroxyapatite from value pH synthesis

pH	6.50	7.00	8.00	9.00	10.00	11.00	12.00	13.00
D, Å	226.8	226.8	226.8	181.4	181.4	181.4	151.2	151.2

Under the received data, it is established that with growth pH synthesis the size of crystalline particles decreases. It, possibly, is connected with growth of a supersaturation of system rather hydroxyapatite at increase pH and formations at the initial stage of crystallisation of a great number of small germs.

Results of IK-spectroscopy are in the consent with data Rentgeno-phase analysis. On spectra of samples absorption strips only hydroxyapatite are shown, phosphatic groups in which structure are partially replaced by carbonates-ions to what presence on spectra of strips with minima in the field of 1400-1450 sm^{-1} (fig. 5).

Thus, all samples received at pH ≥ 7.00, are presented carbonate substitute hydroxyapatite the V-type which particles in a deposit look like units of the various size and consist of the smallest crystalline particles.

For data acquisition about a parity of Ca/P in the received samples, spent quantitative definition of structure supernatant liquids.

It is established that at increase pH residual concentration of Ca and phosphate of ions in supernatant liquids decrease. The strongest change of concentration is observed in an interval pH from 5.50 till since in these conditions there is a phase transition brushite in hydroxyapatite. At the further increase pH synthesis insignificant reduction of residual concentration sediment ions that is connected with growth of degree of sedimentation of apatite and hobby sediment ions in the firm phase which weight accrues at increase alcalinity environments is observed.

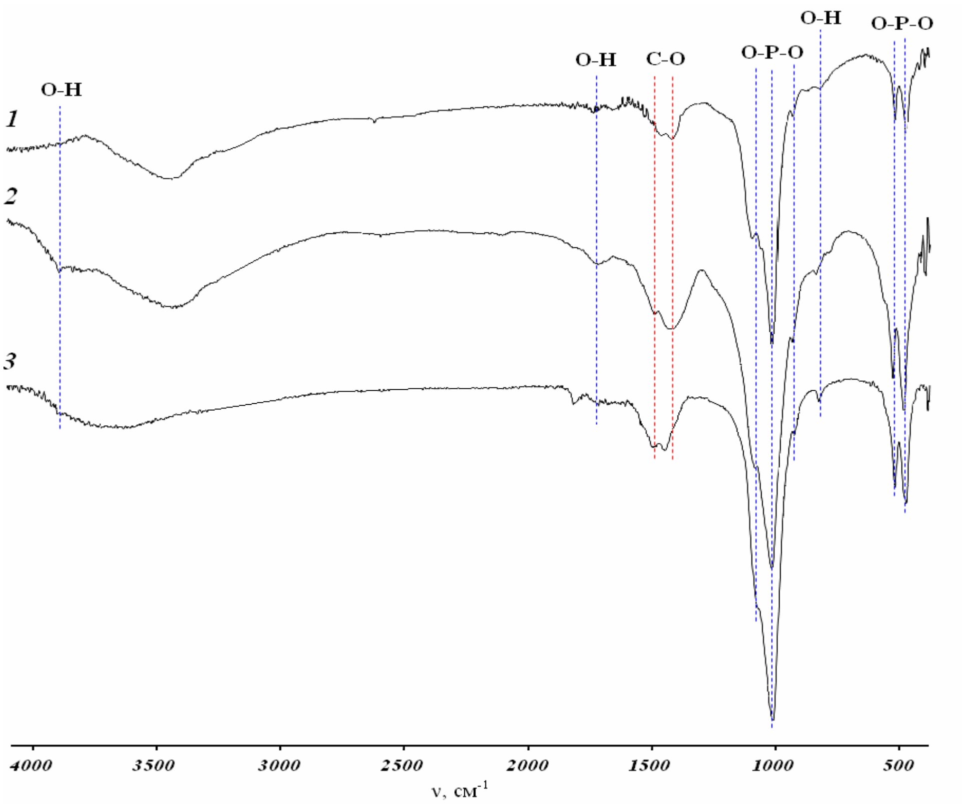


Fig. 5. IK-spectrum of the samples received by sedimentation: 1 – at pH=6.50, 2 – at pH=9.00, 3 – at pH=13.00 (a phase – hydroxyapatite)

Observable laws are caused by increase of a supersaturation of system on the basic phosphate of calcium at increase pH a solution.

On the basis of the data of the analysis of a liquid phase, it is established that at pH = 5.50 the phase with a parity of Ca/P ≈ 1.00 is formed that corresponds stoichiometry brushite. At values pH = 6.00÷11.00 calcium-scarce hydroxyapatite with a parity of Ca/P <1.67 crystallizes. At pH = 12.00 the increase pH till 13.00, possibly is formed stoichiometrical hydroxyapatite with a parity of Ca/P = 1.67, and, calcium-superfluous гидроксилапатита leads to formation, the parity of Ca/P in which is equal 1.70. Hence, optimum conditions of reception hydroxyapatite correspond to a range pH = 12.00÷13.00.

The important characteristic of phosphates of calcium is their ability to dissolution in solutions of various acidity. For studying of solubility of images hydroxyapatite, received at various pH environments, spent their dissolution in a solution 0.01 moth/l HCl within 60 minutes.

It is established that all samples received in experiments, have the similar curves of dissolution differing with values maximum pH which is reached in the course of dissolution. It testifies to differences in structure of the synthesized samples. So, pH systems from pH synthesis hydroxyapatite it is possible to allocate 3 areas for dependences of final value (fig. 6):

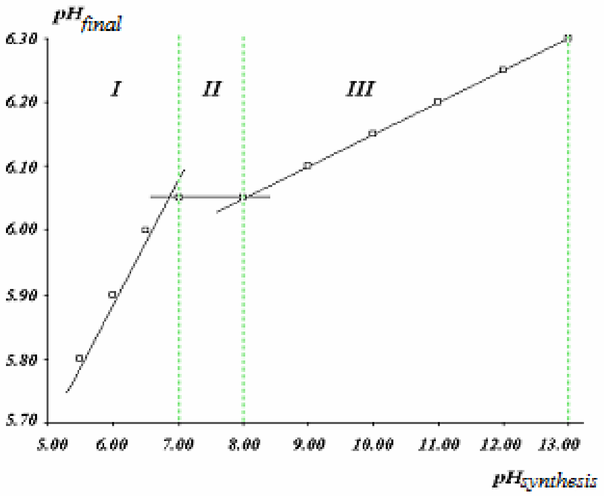


Fig. 6. Diagram of dependence pH final from pH synthesis (t=60 minutes)

I. In an interval $pH_{synthesis}$ = 5.50÷6.50 increase of final value pH systems is observed. It can be connected with change of structure of dissolved substance: brushite (sour phosphate) passes in calcium-scarce гидроксилапатит; in its structure, besides phosphate – and hydrophosphates-ions, are present It - which pass in a solution at dissolution and cause increase pH;

II. In a range $pH_{synthesis}$ = 7.00÷8.00 changes final pH systems it is not noticed that, in our opinion, testifies to absence of changes in apatite structure;

III. Increase final pH systems at dissolution of the samples received at $pH_{synthesis}$ = 8.00÷13.00, is possibly caused by transition calcium-scarce hydroxyapatite in stoichiometrical at which structure there are only calcium ions, phosphates-ions and ions OH^-.

Thus, in process of increase pH synthesis the structure of a firm phase changes as follows: брушит> calcium-scarce hydroxyapatite > stoichiometrical hydroxyapatite. In the same sequence solubility of samples changes.

Conclusions.

- A series hydroxyapatites is received at a variation pH the reactionary environment in an interval 4.00÷13.00.

- It is established that the phase structure of the deposits received at various value pH changes: at pH = 5.50 crystallizes brushite; at pH = 6.00÷6.50 – a mix brushite and hydroxyapatite; at pH = 7.00÷11.00 – calcium scarce hydroxyapatite; at pH> 12.00 – stoichiometrical hydroxyapatite.

- It is shown that at increase pH the reactionary environment the weight of a deposit, the maintenance Ca^2 and PO_4^{3-}, and also a parity of Ca/P in it increases.

- It is revealed that in process of increase pH synthesis the structure of a firm phase changes as follows: brushite > calcium-scarce hydroxyapatite > stoichiometrical hydroxyapatite. In the same sequence solubility of samples changes.

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