

Definition of parameters of crystallization at formation brushite

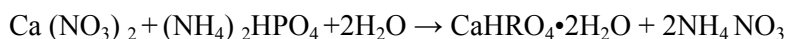
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Participation in processes of formation and degradation of firm fabrics, biocompatibility, bioactivity brushite cause necessity of studying of laws and features of its crystallization [Barinov, 2010, Veresov, 2004, Danilchenko, 2007]. In the present work results theoretical and an experimental research of influence of parameters crystallization and synthesis conditions on possibility and laws of process of sedimentation of two-water hydrophosphate of calcium, its morphology and disperse structure are presented environment.

For an establishment of laws of crystallization brushite synthesis in which basis reaction lies has been carried out:



System studying is spent at equimolar concentration of solutions $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4$ at room temperature.

By results of experiment by Ik-spectroscopy methods (fig. 1) and optical microscopy of the deposits received at synthesis from solutions with concentration of 10 and 25 mmol/l, it is established that at sedimentation during the initial moment of time are formed small crystals brushite (fig. 2) which at deposit maturing are mainly transformed in hydroxyapatite (fig. 2).

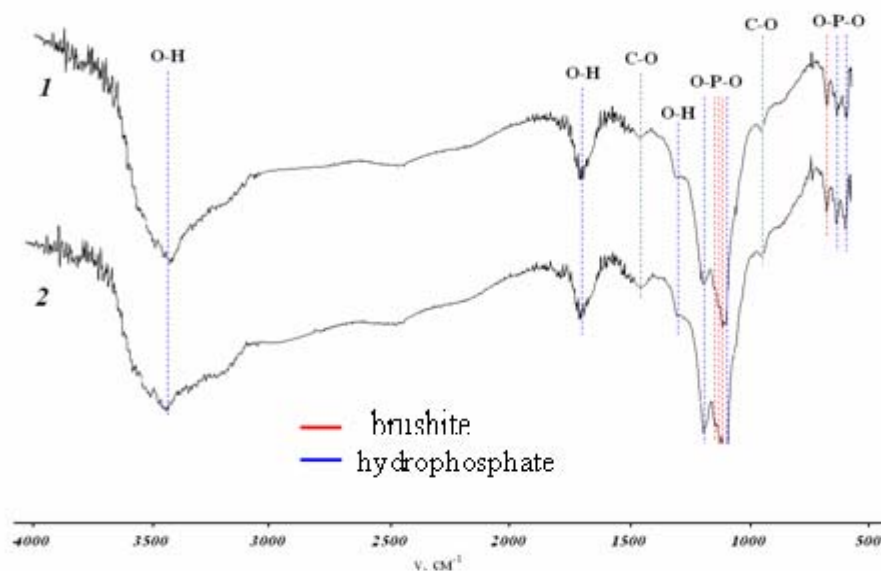


Fig. 1. IK-spectra of the samples received by sedimentation from systems: 1 – With $(\text{Ca}^2, \text{HPO}_4^{2-}) = 25$ mmol/l; 2 – With $(\text{Ca}^2, \text{HPO}_4^{2-}) = 10$ mmol/l

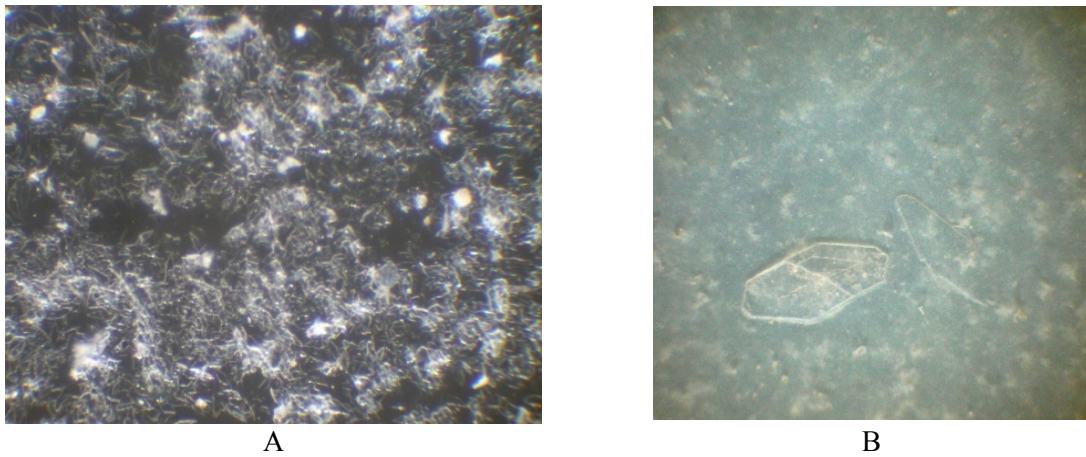


Fig. 2. Photos of particles brushite, received from a solution with $C_{\text{ish}}=10$ mmol/l: A – at the moment of draining, B – after 2 days of maturing

In a material which has been selected from system after phase maturing in a solution within two days, not numerous extended large rhombic crystals brushite in a matrix small crystals hydroxyapatite are found out.

In case of higher initial concentration of ions of calcium and phosphates-ions (With ≥ 50 mmol/l) formed deposits are presented brushite that is confirmed by methods of IK-spectroscopy and X-ray photography the analysis. Maturing of the besieged firm phase was reduced to growth of originally formed germinal crystals of two-water hydrophosphate of calcium (fig. 3). Formed particles have the form of the large extended plates with some defects on a surface in the form of grooves and having chopped off on edges (fig. 3)

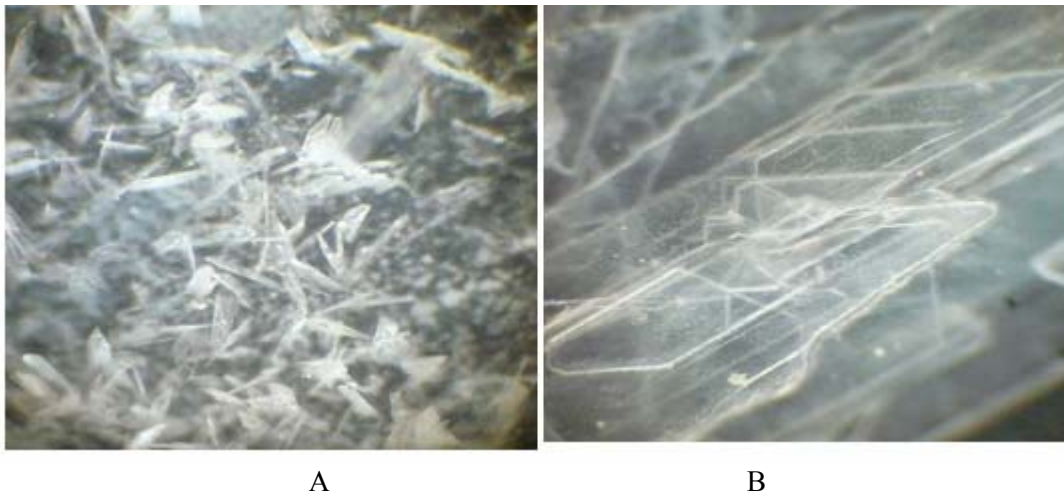


Fig. 3. Photos of particles brushite, received from a solution with $C_{\text{ish}}=50$ of mmol/l: A – at the moment of draining; B – after 2 days of maturing

Research by a method of optical microscopy of the given samples, has allowed to establish that as a result of deposit keeping under a uterine solution within one days of a particle small lamellar crystals brushite which at increase in time of maturing grow represent, and the greatest growth occurs in a direction of one of axes in such a manner that the parity of length of a crystal to its width makes approximately 10:1.

At the analysis of dependence of weight of a deposit from crystallization time, it is possible to tell that the exit brushite in the given conditions doesn't change at deposit keeping under a uterine solution more than two days. The carried out chemical analysis supernatant liquids has shown that the residual maintenance of ions of Ca^{2+} and HPO_4^{2-} in a solution very slightly decreases eventually.

Almost not changing after two days of crystallization residual concentration of Ca^{2+} and HPO_4^{2-} and the calculated degrees of transformation allow to draw a conclusion that the keeping time, exceeding two days, slightly influences crystallization process, i.e. balance between a liquid phase and a deposit is established in this time. The calculated parities of Ca/P changing from 1.08 to 1.06, confirm that a firm phase is brushite.

At a following stage of work influence researches pH on phase structure of deposits are conducted environments.

According to the IK-spectroscopy data (fig. 5), sedimentation brushite occurs enough in a narrow interval, namely from pH from 5.00 till. At shift pH in more alkaline area there is a joint loss of two-water hydrophosphate of calcium and hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$ up to pH=7.00. At the further increase pH crystallizes monophase hydroxyapatite.

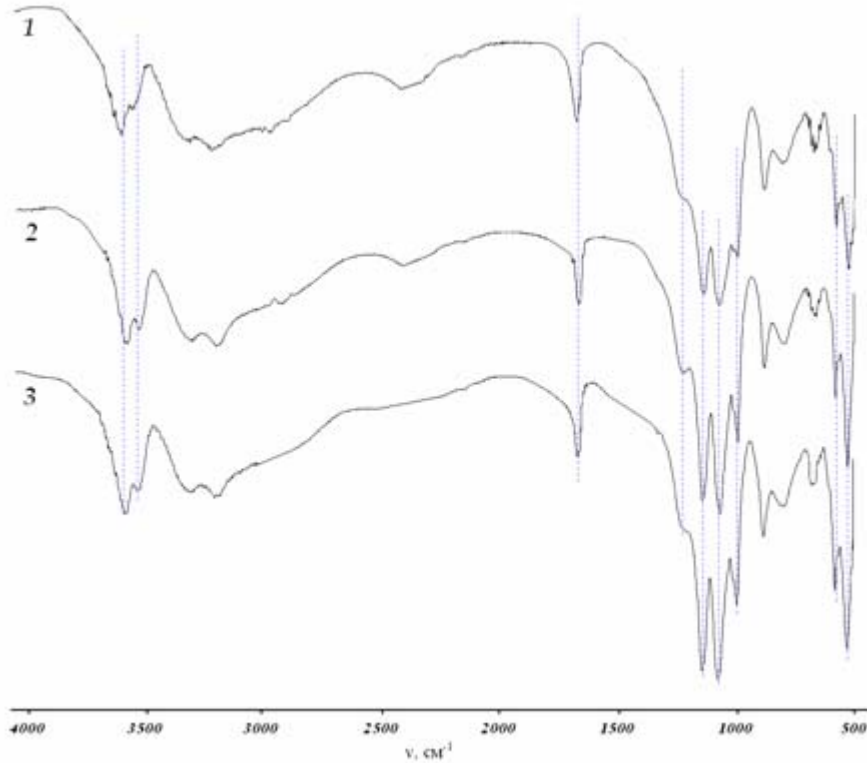


Fig. 4. IR -spectra of samples brushite, received through: 1 – 1 days; 2 – 3 days; 3 – 9 days

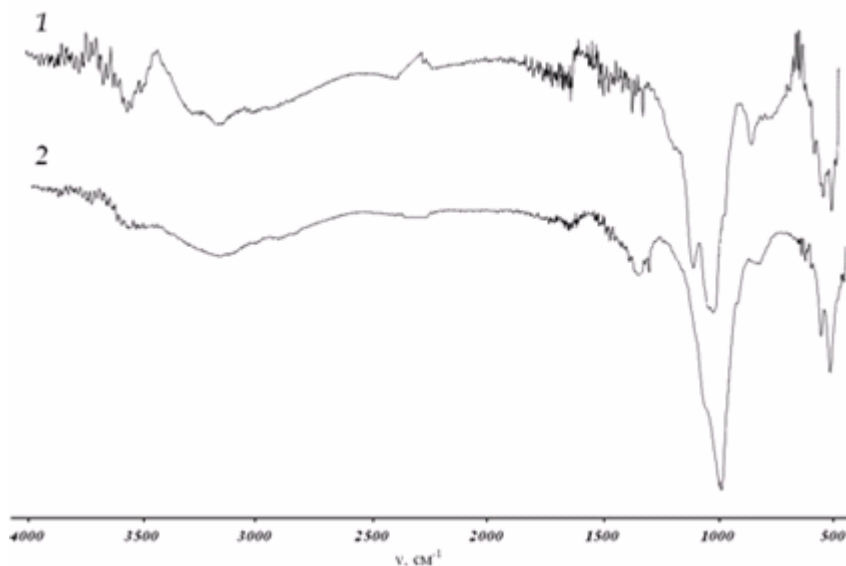


Fig. 5. IR -spectra of the samples received by sedimentation from systems With $(Ca^2, HPO_4^2)_{n_{ex}}=50$ mm at: 1 – pH = 6.50, 2 – pH = 8.00

Research by a method of optical microscopy of the samples who have been selected at the moment of draining of reagents and after two days of crystallization at $pH_{n_{ex}}=5,0$ and $6,0$ has shown that during the

initial moment of time are formed small crystals brushite which at deposit maturing grew and turned to the thin extended plates (fig. 6).

In a range pH from 6.5 to 7.0 after maturing the phase is presented by crystals бpушита in a matrix small crystals hydroxyapatite (fig. 6). In case of higher reference values pH (≥ 8.0) the GA crystallizes in the form of a continuous opaque film with the whitish shade, fissuring at drying.

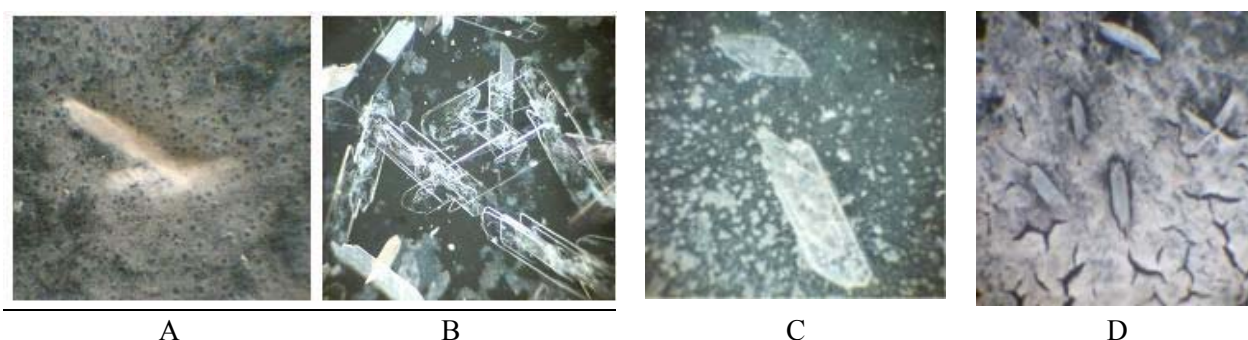


Fig. 6. Photos of particles pH=6.0: A – at the moment of draining; B – after 2 days of maturing pH=7.0: C – at the moment of draining; D – after 2 days of maturing

Data of the chemical analysis testifies to changes of phase structure of deposits supernatant liquids also. Analyzing the data, it is possible to tell that the sharpest change of residual concentration of Ca and P in a solution occurs in the range of $5.5 > \text{pH} > 7.0$. The Plausible reason of increase of maintenances of Ca and P in a deposit is process of crystallization monophasе brushite in a range from 5.5 till then joint formation of two-water phosphate of calcium and hydroxyapatite is observed. With increase pH the system becomes more supersaturate hydroxyapatite and therefore, at $\text{pH} > 7.0$ considerable changes of residual concentration don't occur.

The diagram of dependence of weight of the received deposit from a reference value of acidity of environment shows that the firm phase brushite is formed at $\text{pH} \geq 5.0$. Reduction of products of crystallization in a range pH from 6 to 7 speaks about joint presence at a firm phase brushite and GA. The further increase in weight of a deposit is caused by that the system supersaturate in relation to hydroxyapatite, hence, occurs crystallization monophasе hydroxyapatite. The sharp increase in a parity of Ca/R at $\text{pH} > 6$ says that the firm phase in the given interval isn't brushite. Further influence of an order of draining of solutions has been studied.

It is established that that the deposits received by a way addition of solution $\text{Ca}(\text{NO}_3)_2$ to solution $(\text{NH}_4)_2\text{HPO}_4$ are presented brushite whereas at a return order of draining of reagents, as a part of firm phases crystallizing in studied conditions in common are present brushite and hydroxyapatite.

The method of optical microscopy has allowed to establish that crystals brushite in both cases have the form of the thin extended plates, with some defects on a surface in the form of furrows and having chopped off on edges. However as a part of the samples which formation occurred at addition a solution of hydrophosphate of ammonium to a solution of nitrate of calcium, besides lamellar crystals brushite there are the various form units hydroxyapatite.

Settlement sizes of degree of course on calcium and hydrophosphates-ions of reaction of sedimentation in cases of a different order of draining of reagents have close values. Possibly, incomplete course of process formation is caused by solubility of a firm phase. The parity of Ca/P in the received samples close by 1.00 that corresponds stoichiometе brushite. Also influence of speed of draining of reagents on characteristics of crystallizing substance of process of sedimentation is studied. The analysis spent by a method of Ik-spectroscopy, has shown that the samples received as by fast addition of solution $\text{Ca}(\text{NO}_3)_2$ to solution $(\text{NH}_4)_2\text{HPO}_4$, and slow draining of reagents (on drops), are formed brushite.

Research of samples by a method of optical microscopy has allowed to establish that, in comparison with besieged at fast draining of reagents, small crystals, received by a way addition solutions on drops, have the smaller sizes. Particles brushite in the form of thin needles and plates form units of the various sizes. Possibly, it is connected with a high supersaturation in system, and as consequence, formation of set of germinal skeletal crystals brushite which, incorporating in large units, drop out in a deposit.

By the received results it is possible to draw a conclusion that at reception brushite a way addition reagents on drops degree of course of reaction more than in the samples synthesized by draining of solutions, and the received parity of Ca/R in a deposit makes 1,02 that is closer to theoretical stoichiometе for brushite 1,00.

Conclusions

1. Crystallization possibilities brushite by $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ from system $\text{Ca}(\text{NO}_3)_2 - (\text{NH}_4)_2\text{HPO}_4 - \text{H}_2\text{O}$, containing equivalent quantities of ions of Ca^{2+} and HPO_4^{2-} are experimentally defined.
2. Influence on phase structure of a deposit and the characteristic of process of sedimentation of experimental conditions (concentration of initial components are investigated; crystallization time; pH crystallization environments; an order of draining of solutions; speed of draining of reagents).
3. Optimum conditions for reception of crystals brushite are picked up: crystallization time 2 days; concentration of initial reagents $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4 - 50 \text{ mmol/l}$; an order of draining of initial solutions: $\text{Ca}(\text{NO}_3)_2$ to a solution $(\text{NH}_4)_2\text{HPO}_4$; pH = 5.0–6.0.

References

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