THERMAL ANALYSIS OF CALCIUM PHOSPHATES DEPOSITED FROM WATER SOLUTIONS OF HYDROMONOPHOSPHATE AND SODIUM DIPHOSPHATE

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Introduction: Recently, there has been an interest in calcium phosphate materials based on nanocrystalline hydroxyapatite, which due to thermodynamic instability are inclined to accelerated biodegradation and assimilation by a living organism. Amorphous calcium phosphate compounds similar in composition to natural bone tissues, i.e. hydroxyapatite should serve as an alternative to amorphous hydroxyapatite.

The purpose of the study was to obtain materials including amorphous hydroxyapatite, establish their nature, to identify the conditions under which they are formed, and to develop a method for their production.

Materials and methods. Aqueous solutions of sodium diphosphate Na$_4$P$_2$O$_7$ and sodium hydromonophosphate were used for synthesize research objects. Thermal analysis of the obtained products was carried out on the derivatograph of the system MOM Q-1500. Diffractograms were recorded on a DRON-3 diffractometer using CuK$_\alpha$ and CoK$_\alpha$-radiations.

Results. Substances precipitated from a solution of hydromonophosphate in the presence of 5% sodium diphosphate under high temperature conditions behave differently than hydroxyapatite. Thus, a narrow and quite intense exoeffect appears on the corresponding DTA curve above 600°C. The latter indicates that transformations that are accompanied by the release of heat take place in the sample. In calcium phosphates precipitated in the presence of even more sodium diphosphate, exothermic transformations are also observed. Temperature and the value of thermal effects on the corresponding DTA curves depend on the samples composition. The exoeffects of products precipitated from solutions in the presence of (30-40)% sodium diphosphate have a maximum value and temperature. Since both these parameters serve as a measure of disorder and thermodynamic instability of substances, it can be assumed that the corresponding phosphates are maximally amorphized.
Results of X-ray analysis showed that in samples heated above the temperature of thermal effects, there are two-three phases: hydroxyapatite, tricalcium phosphate and calcium diphosphate. The first salt is a part of the products of thermal transformations of those substances that were obtained from solutions with a sodium diphosphate content of not more than 30%. As the precipitated substances are enriched with sodium diphosphate, the proportion of hydroxyapatite in products of transformation decreases. Tricalcium phosphate is present in all samples apart from the precipitated amorphous calcium diphosphate formed as a result of heating. This salt is also present in significant amount among the products of thermal transformations of hydroxyapatite, which may be a consequence of transformations of the nonstoichiometric part of the substance. As precipitated amorphous substances are enriched with calcium diphosphate, the proportion of \( \text{Ca}_3(\text{PO}_4)_2 \) in thermal transformation products first increases, reaches a maximum in samples corresponding to substances precipitated in the presence of (15-20)% sodium diphosphate, and then decreases. The amount of crystalline \( \text{Ca}_2\text{P}_2\text{O}_7 \) only increases, which is quite natural.

The existence of exothermic effects on DTA curves indicates that a complex sequence of transformations occurs in precipitated phosphates upon heating. Their result is ordering, connected both with the consolidation of the same molecular forms into separate crystals, and the corresponding transport processes.

**Conclusion.** Presence of tricalcium phosphate transformations among the products and the extreme nature of the curve corresponding to the formation of \( \text{Ca}_3(\text{PO}_4)_2 \), indicate that the interaction between the main components of the precipitated substances, in addition to transformations of the non-stoichiometric part of hydroxyapatite, takes place according to the scheme

\[
2\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{Ca}_2\text{P}_2\text{O}_7 = 4\text{Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{O}
\]

This reaction involves water allocation. However, no noticeable gravitational effects were observed near the temperatures corresponding to the exoeffects on DTA curves. Therefore, it can be assumed that the interaction between hydroxyapatite and calcium diphosphate occurs earlier, possibly even during dehydration, i.e. at temperatures below \((400-500)\)°C.

**Prospects for further research.** It has already been noted that calcium phosphates, which include hydroxyapatite are of interest for medicine,
particularly, for dentistry and orthopedics. Amorphized materials obtained during the implementation have advantages in this respect - due to their nature they have to be highly bioactive and easily assimilated by organism. The presence of diphosphate can affect the efficiency of materials in the biomedical terms. Another possible area of practical use of amorphous apatite-containing substances is ecology. Amorphous calcium phosphates having a large specific surface area and having a high affinity for multivalent metals should show sorption activity to polyvalent metals. Amorphous apatite-containing substances also bind some kinds of radionuclides in aqueous solutions.

References:

Accepted for printing on 15 Dec 2017