

REACTION CHEMISTRY OF HYDROXYAPATITE: FORMATION AND DECOMPOSITION

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Abstract. The solid state formation of stoichiometric hydroxyapatite (HAp) was investigated in detail by heating the $\text{Ca}_3(\text{PO}_4)_2\text{-CaO}$ mixture and $\text{Ca}_4(\text{PO}_4)_2\text{O}$ in the presence of water vapour. HAp was an exceptionally thermally stable hydroxide even at high temperatures above 1000 °C and at low water vapour pressures. New cementing materials consisting of $\alpha\text{-Ca}_3(\text{PO}_4)_2$, $\alpha\text{-Ca}_3(\text{PO}_4)_2 + \text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} + \text{CaCO}_3$ were found and clarified with respect to the hardening accompanying the formation of calcium-deficient hydroxyapatite (DAP), hydration reactions with and without additives, and mechanical strength of hardened products. The conversion of sparingly water-soluble $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and a calcium silicate mixture into DAP was successfully conducted. Thermal decomposition characteristics of DAP, HAp, $\text{HAp} + \text{SiO}_2$, and $\text{HAp} + \text{Ca}_2\text{P}_2\text{O}_7$ were elucidated in detail.

Key words: hydroxyapatite, solid state formation, thermal decomposition, apatitic cement.

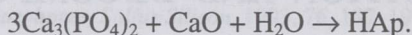
INTRODUCTION

Preparation and decomposition reactions of hydroxyapatite, as well as those of fluorapatite, are important. These reactions have become of increasing interest in connection with various developments of functional materials of calcium phosphate. Details of hydroxyapatite chemistry have been often reviewed by various researchers including Kanazawa [1]. The composition of hydroxyapatite is given stoichiometrically as $\text{Ca}_{10}(\text{PO}_4)_2(\text{OH})_2$ (referred to as HAp) and calcium-deficiently as $\text{Ca}_{10-X}(\text{HPO}_4)_X(\text{PO}_4)_{6-X}(\text{OH})_{2-X} \cdot n\text{H}_2\text{O}$; $0 < X \leq 1$ (DAP). HAp-based

ceramics are applied to bioactive materials with good biocompatibility, and powdery and porously hardened DAp materials to bioactive materials, adsorbents for biological macromolecules, ion-exchangers for heavy metal ions, and catalysts for the decomposition of alcohols and chlorine-containing organic compounds. The present paper presents the formation and decomposition reactions involving HAp and DAp investigated so far by the authors.

SOLID STATE FORMATION

Ca₃(PO₄)₂-CaO-H₂O vapour: The high temperature formation of HAp in water vapour has been already reported by many researchers. The formation reaction using Ca₃(PO₄)₂ is expressed as follows:



The equilibrium of this reaction is governed thermodynamically only by water vapour pressure ($p_{\text{H}_2\text{O}}$). For example, the equilibrium $p_{\text{H}_2\text{O}}$ at 1000°C is 10⁻² mmHg [2]. HAp is an exceptionally thermally stable hydroxide. The authors investigated the reaction in detail also under various conditions of mixing ratio of the reactants, $p_{\text{H}_2\text{O}}$, heating temperature, and time as shown in Figs. 1 and 2 [3].

HAp was formed even in an atmosphere ($p_{\text{H}_2\text{O}} = 2.4$ mmHg) dried with silica gel. The conversion increased with increasing $p_{\text{H}_2\text{O}}$, temperature, and time. Increasing mixing ratio of Ca₃(PO₄)₂/CaO was also effective as the reaction contact area increased. Excess CaO after runs could be removed with NH₄Cl aqueous solution. The obtained curves obeyed the Shinriki-Kubo equation derived for solid state reactions in a similar manner as the Jander equation. According to Arrhenius plots of rate constants obtained at different temperatures, an apparent activation energy for the HAp formation was 25 kcal/mol.

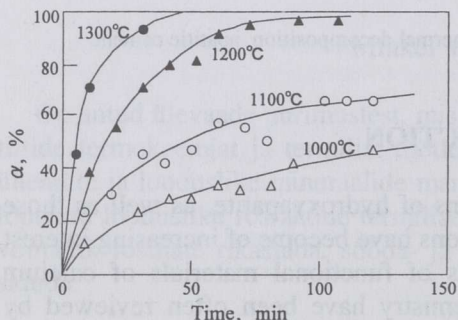


Fig. 1. Effect of temperature on the conversion (α) of Ca₃(PO₄)₂ into HAp. 3Ca₃(PO₄)₂/5CaO mixture, $p_{\text{H}_2\text{O}}$ 23 mmHg.

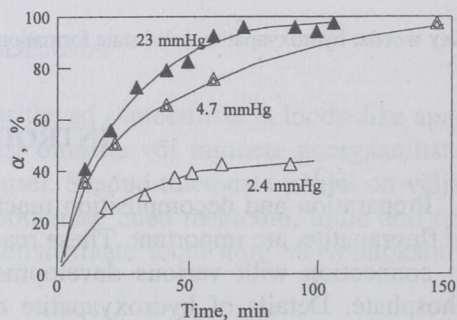


Fig. 2. Effect of $p_{\text{H}_2\text{O}}$ on the conversion (α) of Ca₃(PO₄)₂ into HAp. 3Ca₃(PO₄)₂/5CaO mixture, temperature 1200°C.

additives such as NH_4Cl , NaCl , NaH_2PO_4 , $\text{CH}_3\text{COONH}_4$, etc. The hydration conversion of $\alpha\text{-Ca}_3(\text{PO}_4)_2$ into DAP under initial conditions of pH 6.0 and 3 h treatment at 40°C was adjusted to 0–90% by additives and setting times of 4–30 min [8].

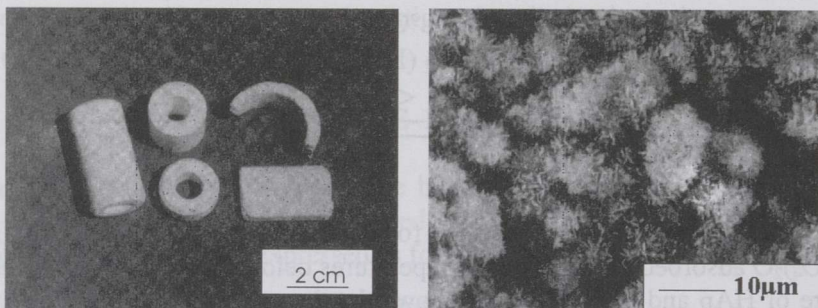
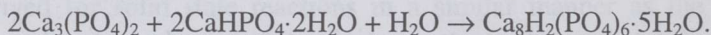
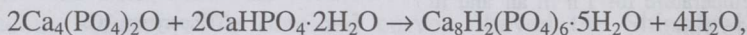


Fig. 4. Photographs of hardened DAP. Left: hardened DAP (left 3 pieces) at 80°C and sintered DAP (right 2 pieces) at 1100°C . Right: microstructure of hardened DAP.

$\alpha\text{-Ca}_3(\text{PO}_4)_2\text{-CaHPO}_4\cdot 2\text{H}_2\text{O}$: Since the finding of the hydraulicity of $\alpha\text{-Ca}_3(\text{PO}_4)_2$ [5], the system $\text{CaO-P}_2\text{O}_5$ has become of interest especially in the field of biomaterials as a new cementing composition system. Brown and Chow [9] presented independently the $\text{Ca}_4(\text{PO}_4)_2\text{O-CaHPO}_4\cdot 2\text{H}_2\text{O}$ combination, and the present authors have also proposed the $\alpha\text{-Ca}_3(\text{PO}_4)_2\text{-CaHPO}_4\cdot 2\text{H}_2\text{O}$ combination [10]. The overall hydration reactions of these were expressed as follows:



Setting times in the latter system were adjusted to 9 min–2 h by changing the mixing ratio of the reactants. Mechanical strengths of the resulting hardened bodies increased up to 20 MPa (wet) and ca. 40 MPa (dry) in compressive strength in a 0.9% NaCl physiological solution.

$\text{CaHPO}_4\cdot 2\text{H}_2\text{O-CaCO}_3$: The conversion of $\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$ into octacalcium phosphate or DAP or HAP in solution is made by continuously controlling an alkaline medium. The resulting products are obtained as powder because the reaction system has to be stirred for the reaction to proceed. However, $\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$ mixed with CaCO_3 transformed to octacalcium phosphate or DAP without stirring [11]. As a result, hardened products were obtained. CaCO_3 seemed to act as a “solid pH-buffer”. Figure 5 shows the conversion fraction of $\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$ in the system with and without F^- . The addition of F^- was very effective for the acceleration of the conversion, but not for the hardening. Reaction products were octacalcium phosphate at 50°C and carbonated DAP at 80°C [12]. The resulting hardened bodies have 70–80% porosity and 0.3–1.5 MPa diametral tensile strength.

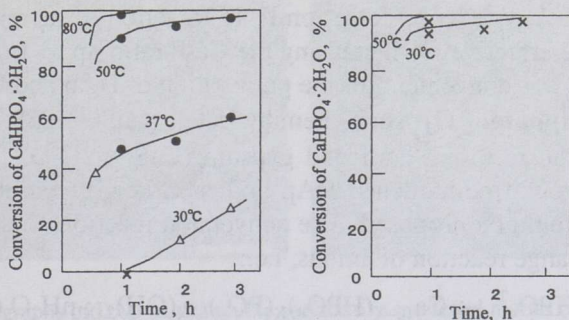
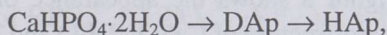


Fig. 5. Hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in the system $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}-\text{CaCO}_3-\text{H}_2\text{O}$ with F^- (right) and without F^- (left). ● Tightly hardened, Δ weakly hardened, × non-hardened.

CONVERSION OF CALCIUM PHOSPHATE, SULPHATE, AND SILICATE INTO HYDROXYAPATITE

Calcium phosphate: The hydrolysis conversion of brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) into DAp and HAp was investigated on the basis of the following two-step idea [13]:



where the first step (I) is the structural change of brushite into apatite with a Ca/P ratio of 1.50 and the second (II) subsequent compositional increases up to $\text{Ca/P} = 1.67$ keeping the apatite structure. The maximum reaction rate of Reaction I occurred around pH 8. Hydrolysis time for the complete conversion at pH 8 was within 2.5 h at 40°C, 1 h at 60°C, and only 5 min at 80°C. The Ca/P ratios of DAp thus formed were about 1.50 (40°C, 3 h) and 1.60 (80°C, 5 h). The value 1.60 seemed to be a limit as shown in Fig. 6. The addition of Ca^{2+} in an attempt to increase the Ca/P ratio was highly inhibitory to the hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ as shown in Fig. 7. In order to increase the Ca/P ratio, DAp was once separated from the mother liquor of Reaction I, and treated in alkaline

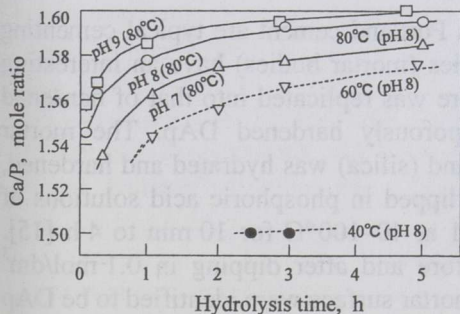


Fig. 6. Increases in Ca/P ratio of DAp formed in Reaction I as a function of pH and temperature.

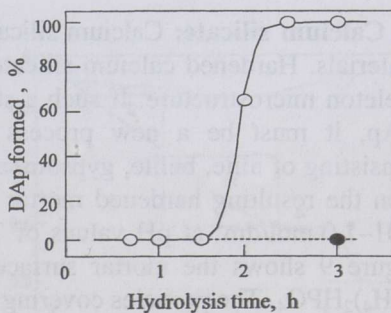
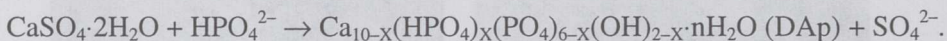


Fig. 7. Conversion of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ into DAp with (●) and without (○) addition of Ca^{2+} in Reaction I (40°C, pH 8).

solutions with Ca^{2+} added, i.e., Reaction II. In Reaction II, increasing pH and/or adding Ca^{2+} were effective for increasing the Ca/P ratio up to 1.67 of HAp. This two-step process was convenient for the preparation of DAp and HAp.

Calcium sulphate: Gypsum hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) has good hydraulicity. If the resulting hardened gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) bodies could be converted into crack-free hardened DAp bodies, a new preparation process for hardened DAp would be proposed. The conversion reaction could apparently be given by an exchange reaction of anions, i.e.:



Since the difference in density between $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (2.3 g/cm^3) and DAp ($\sim 3.2 \text{ g/cm}^3$) might cause an occurrence of cracks during the conversion, the preparation of crack-free DAp bodies was not easy. Runs were carried out by dipping hardened gypsum bodies (porosity 24%, compressive strength 43 MPa) in $(\text{NH}_4)_2\text{HPO}_4$ solutions of $0.1\text{--}1.0 \text{ mol/dm}^3$ at temperatures of $80\text{--}160^\circ\text{C}$ [14]. Crack-free DAp hardened bodies with porosities of ca. 60% were obtained by dipping in the solution of 1.0 mol/dm^3 at $100\text{--}140^\circ\text{C}$ for 5 days. However, remarkable increases in porosity, in other words, decreases in strength, were observed. Increasing pH and the concentration of the solution were effective for the crack-free conversion. Figure 8 shows the appearance of DAp bodies with and without cracks and the microstructure of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and DAp hardened bodies.

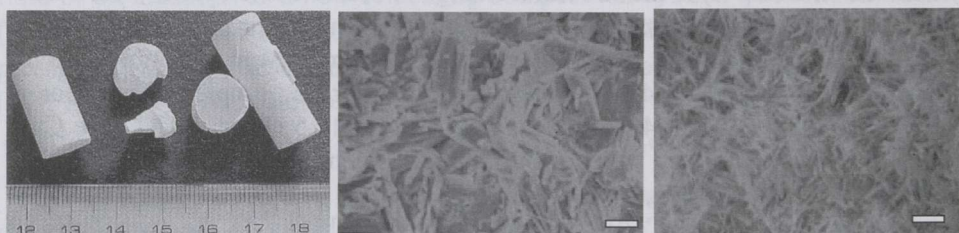


Fig. 8. DAp bodies (left) converted from hardened $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ bodies and SEM microphotographs of hardened $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (middle) and DAp (right). $\equiv 10 \mu\text{m}$.

Calcium silicate: Calcium silicates in Portland cement are typical cementing materials. Hardened calcium silicate bodies (mortar bodies) have an interesting skeleton microstructure. If such a structure was replicated into that of hardened DAp, it must be a new process for porously hardened DAp. The mortar consisting of alite, belite, gypsum, and sand (silica) was hydrated and hardened, then the resulting hardened mortar was dipped in phosphoric acid solutions of $0.01\text{--}1.0 \text{ mol/dm}^3$ at pH values of $7.5\text{--}11$ at $40\text{--}100^\circ\text{C}$ for 10 min to 4 h [15]. Figure 9 shows the mortar surfaces before and after dipping in 0.1 mol/dm^3 $(\text{NH}_4)_2\text{HPO}_4$. The particles covering the mortar surface were identified to be DAp with scaly, porous, and submicron square particles of about 100 nm thickness. The coverage became clearer under the conditions of pH 10 and 100°C for 4 h in 1.0 mol/dm^3 H_3PO_4 .

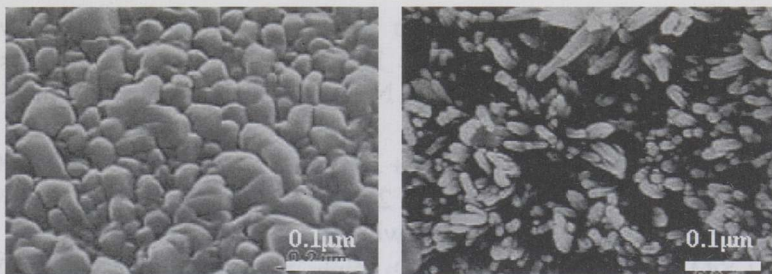


Fig. 9. SEM photographs of DAp (right) on the surface of a hardened mortar (left). (60 °C for 4 h in 0.1 mol/dm³ (NH₄)₂HPO₄ solution).

THERMAL DECOMPOSITION

DAp: Figure 10 shows the TG and DTA curves of DAp. The thermal changes of DAp were summarized as follows [16]:

I: Evolution of adsorbed H₂O

II: Liberation of lattice H₂O

Appearance of an ESR signal above 180 °C

III: Condensation of HPO₄²⁻ (2HPO₄²⁻ → P₂O₇⁴⁻ + H₂O↑)

Formation of apatite with a composition Ca_{10-x}(P₂O₇)_x(PO₄)_{6-2x}(OH)₂

Increases of the ESR signal up to 520 °C and disappearance at 600 °C

IV: Unidentified

V: P₂O₇⁴⁻ + 2OH⁻ → 2PO₄³⁻ + H₂O↑

Formation of (1 - X)HAp + 3XCa₃(PO₄)₂

In addition, the reaction PO₄³⁻ + lattice H₂O → OH⁻ + 1/2P₂O₇⁴⁻ + 1/2H₂O↑ occurred in the range of 250 to 600 °C. The ESR signal probably arose from trapped electrons in a locally distorted apatite structure induced by the condensation of HPO₄²⁻. Partial fluoridation of DAp inhibited completely the weight decrease above 500 °C [17]. The composition of the resulting apatite was Ca_{10-x}(P₂O₇)_x(PO₄)_{6-2x}F_{2-x}(OH)_x, which was stable even at 1340 °C.

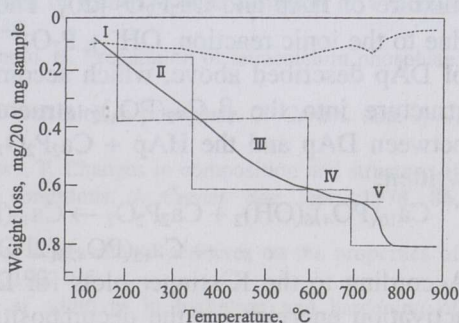
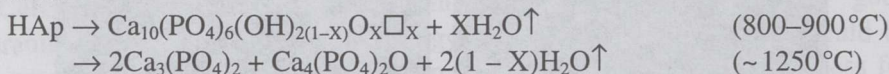
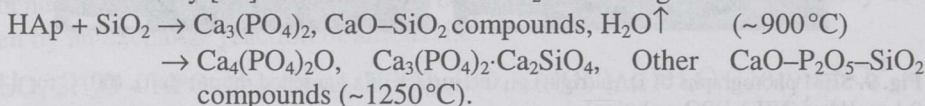


Fig. 10. TG (—) and DTA (· · ·) curves of DAp.

HAP with and without SiO₂: HAP is an exceptionally thermally stable hydroxide as mentioned above. Figure 11 shows the thermal decomposition of HAP and a mixture of HAP + SiO₂ in N₂. The self-decomposition of HAP was given as



where \Box is vacancy [18]. The reaction with SiO₂ could be given as



The HAP-SiO₂ reaction increased with increasing the amount of SiO₂ addition; however, it decreased remarkably with introducing water vapour [19]. The thermal stability of the apatite structure was increased significantly by partial substitutions of F⁻ for OH⁻ as shown in Fig. 12.

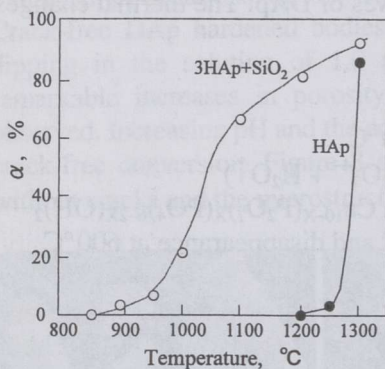


Fig. 11. Decomposition (α) of HAP with and without SiO₂ after thermal treatment for 3 h in N₂.

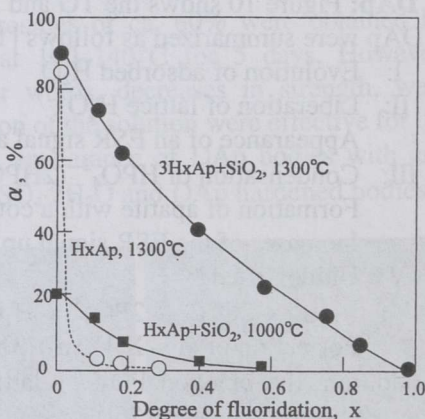
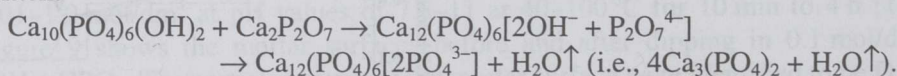


Fig. 12. Decomposition (α) of fluoridated HxAp ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-x}\text{F}_x$) with and without SiO₂ after thermal treatment for 3 h in N₂.

HAP-Ca₂P₂O₇: Figure 13 shows the TG and DTA curves for DAp and a mixture of HAP and Ca₂P₂O₇ [20]. The weight loss of DAp at 700–900°C was due to the ionic reaction, $\text{OH}^- + \text{P}_2\text{O}_7^{4-} \rightarrow 2\text{PO}_4^{3-} + \text{H}_2\text{O}\uparrow$ as well as in the case of DAp described above, which accompanied the decomposition of the apatite structure into the $\beta\text{-Ca}_3(\text{PO}_4)_2$ structure. From the similarity of TG curves between DAp and the HAP + Ca₂P₂O₇ mixture, the following reaction can be written:



According to the Kissinger plots for DTA peaks around 700–900°C, apparent activation energies for the decompositions were 90 kcal/mol for DAp and 50 kcal/mol for the HAP-Ca₂P₂O₇ mixture.

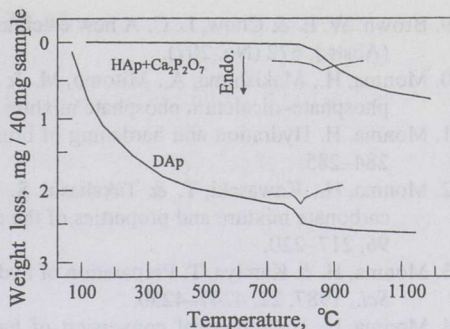


Fig. 13. TG-DTA curves for a HAp-Ca₂P₂O₇ (1:1 mole ratio) mixture and DAp.

SUMMARY

Stoichiometric and calcium-deficient hydroxyapatites (HAp and DAp, respectively) have been reviewed with respect to the solid state formation, hydrolysis formation accompanying hydraulicity, conversion of sparingly water-soluble calcium compounds, and thermal decomposition characteristics. HAp was confirmed to be an exceptionally thermally stable hydroxide. The solid state formations of HAp were investigated in detail by heating the Ca₃(PO₄)₂-CaO mixture and Ca₄(PO₄)₂O in the presence of water vapour. New cementing compositions of α-Ca₃(PO₄)₂, α-Ca₃(PO₄)₂ + CaHPO₄·2H₂O, and CaHPO₄·2H₂O + CaCO₃ were proposed and the hydration reactions and mechanical strengths of hardened products were clarified. The conversions of sparingly water-soluble CaHPO₄·2H₂O and CaSO₄·2H₂O and a calcium silicate mixture into DAp were successfully conducted. Thermal decomposition characteristics of DAp, HAp, HAp + SiO₂, and HAp + Ca₂P₂O₇ were elucidated.

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HÜDROKSÜAPATIIDI REAKTSIOONIKEEMIA: TEKE JA LAGUNEMINE

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On kirjeldatud suure termilise püsivusega hüdroksüapatiidi (HAp) saamist tahkes faasis $\text{Ca}_3(\text{PO}_4)_2$ ja CaO segu või $\text{Ca}_4(\text{PO}_4)_2\text{O}$ kuumutamisel veeauru manulusel. On välja töötatud uued hambatsemendi materjalid, lähtudes $\alpha\text{-Ca}_3(\text{PO}_4)_2$ -st, $\alpha\text{-Ca}_3(\text{PO}_4)_2$ ja $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ või $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ja CaCO_3 segust ning määratud kõvastunud materjalide omadusi mõjutavad tegurid. $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ja kaltsiumsilikaadi segu kuumutamisel saadi kaltsiumi suhtes defitsiitne hüdroksüapatiit (DAP). On kindlaks tehtud DAP, HAp, HAp ja SiO_2 ning HAp ja $\text{Ca}_2\text{P}_2\text{O}_7$ segu termilise lagunemise iseärasused.