

THERMOCHEMICAL REACTIONS IN THE SYSTEMS HYDROXYAPATITE—ALUMINOSILICATE OR SHUNGITE

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Abstract. The reactions in the mixtures of hydroxyapatite with 20% of natural aluminosilicate (nepheline, pseudoleicite, glauconite) or shungite, at temperatures up to 1400 °C, were studied by thermal, XRD and chemical analysis.

The decomposition of hydroxyapatite is enhanced in the mixtures. The reaction of $\text{Ca}_3(\text{PO}_4)_2$ with nepheline and glauconite is almost complete, pseudoleicite reacts partially before the formation of leucite. The calcination product of shungite (quartz, cristobalite) does not react with $\text{Ca}_3(\text{PO}_4)_2$ at temperatures up to 1400 °C. The crystalline phases soluble in 2% citric acid solution are presented in the products of calcination as $\alpha\text{-Ca}_3(\text{PO}_4)_2$ and its solid solutions with $\alpha\text{-Ca}_2\text{SiO}_4$, nagelschmidite, and phases on the basis of $\beta\text{-Ca}_3(\text{PO}_4)_2$.

Key words: hydroxyapatite, aluminosilicate, shungite, thermal reactions up to 1400 °C.

INTRODUCTION

It has been established that aluminosilicates influence conductively the solubility of thermophosphate fertilizers obtained from apatite by sintering process [1]. The aim of this research work was to study the thermal reactions in this process using model systems from synthetic hydroxyapatite (HAp) and concentrates of natural aluminosilicates or shungite.

EXPERIMENTAL

In our experiments, a commercial HAp (95%) and natural aluminosilicate concentrates of nepheline, pseudoleicite and glauconite or shungite were used. The chemical composition of natural minerals is given in Table 1.

To prepare the mixture, 20% (by mass) of silicate was added to HAp. The mixtures were ground and then heated for 1 h in a Pt crucible at the temperatures of 1100, 1200, 1300 and 1400 °C, cooled slowly and ground again carefully.

Table 1

Chemical composition of silicates, %

Mineral	Nepheline (Na, K)AlSiO ₄	Pseudoleicite KAlSi ₃ O ₈ + +KAlSiO ₄	Glaucosite K ₂ O·4(Mg, FeO, Fe ₂ O ₃ , Al ₂ O ₃)· ·10SiO ₂ ·3H ₂ O	Shungite
SiO ₂	54.3	55.7	51.1	59.8
Al ₂ O ₃	22.2	21.5	10.7	3.5
Fe ₂ O ₃ +FeO	3.3	1.1	20.3	0.8
K ₂ O	6.3	15.0	8.9	1.4
Na ₂ O	11.4	0.4	0.1	0.1
MgO	0.2	0.3	4.4	0.3
C	—	—	—	31.5
Weight loss on heating up to 1400 °C, %	1.5	0.9	7.8	17.4*

* Temperature 1000 °C.

The molar ratio of CaO:P₂O₅ in the mixtures varies from 3.16 to 3.18, that of SiO₂:P₂O₅ ranges from 0.77 to 0.90 (Table 2). In the mixture with glaucosite, there is more Fe₂O₃ and MgO, and less Al₂O₃ than in the mixtures with other aluminosilicates. The differences in Me₂O content and Na₂O:K₂O ratio are also notable. The Me₂O content is the smallest in the mixture with glaucosite. Besides, in the mixture with nepheline, Me₂O is presented mainly by Na₂O, in other mixtures by K₂O. The mixture with shungite differs from the others by the highest ratio of SiO₂:P₂O₅, and by the smallest content of Al, Fe and K.

The solubility of P, K, Na and Mg in the 2% citric acid solution of calcined samples (1 g/200 ml, 30 min shaking, 20 °C) was studied by chemical methods. The content of soluble SiO₂ was calculated from the total content of SiO₂ and from the content of SiO₂ in insoluble residue.

Table 2

Chemical composition of calcined mixtures hydroxyapatite + 20% silicate, %

Mineral	Nepheline	Pseudo- leicite	Glaucosite	Shungite
P ₂ O ₅	33.5	34.1	33.7	34.4
SiO ₂	11.7	12.1	10.9	13.1
CaO	42.2	42.4	42.0	42.8
MgO	0.2	0.1	0.9	0.1
Na ₂ O+K ₂ O=Me ₂ O	6.6	6.2	4.2	2.7
Fe ₂ O ₃	0.7	0.2	4.3	0.2
Al ₂ O ₃	4.8	4.7	2.3	1.0
Molar ratio				
Total SiO ₂ :P ₂ O ₅	0.82	0.84	0.77	0.90
Soluble SiO ₂ :P ₂ O ₅ (1400 °C)	0.63	0.32	0.62	0.05

Thermal changes of aluminosilicates and shungite and their mixtures with HAp were studied by thermal analysis (DTA) using MOM and SEIKO equipment. The Pt crucibles, and Al_2O_3 as the reference material, were used for measurements carried out at heating rate $10^\circ/\text{min}$.

X-ray powder diffraction was used to study the phase composition of the calcined mixtures and their insoluble residue in 2% citric acid. Diffraction data were obtained with DRON-4 equipment using Cu radiation (step size 0.03 deg from 20° to $50^\circ 2\theta$).

RESULTS AND DISCUSSION

1. Mixture HAp + nepheline (N)

On the basis of thermal analysis data, N melts at $1150\text{--}1190^\circ\text{C}$. In the same region, a weak endothermic peak appears in the DTA curve of the mixture (Fig. 1).

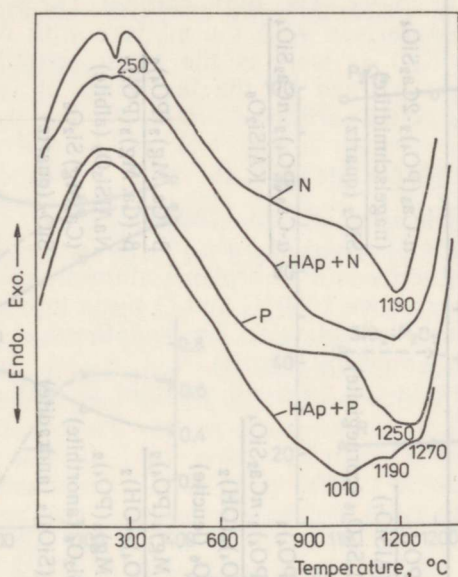


Fig. 1. DTA curves for nepheline (N) and pseudoleicite (P) and for their mixtures with hydroxyapatite (HAp) in N_2 flow with heating rate $10^\circ/\text{min}$ (SEIKO instrument).

From X-ray diffraction data (Table 3) it can be seen that the mixture calcined at 1100°C consists of HAp ($d=2.82, 2.78, 2.72$, ASTM 9-256), $\beta\text{-Ca}_3(\text{PO}_4)_2$ ($d=2.88, 2.614, 3.21$, ASTM 9-169), gehlenite ($d=2.85, 3.03, 2.430$, ASTM 4-0690), and nepheline ($d=3.87, 3.03, 4.16$, ASTM 35-424). The soluble phases are $\beta\text{-Ca}_3(\text{PO}_4)_2$ at $1100\text{--}1200^\circ\text{C}$ and nagelschmidite ($d=2.85, 2.655, 3.88$, ASTM 11-676) at $1300\text{--}1400^\circ\text{C}$. At 1200°C , the insoluble residue contains gehlenite and cornegicite ($d=3.00, 4.18, 4.04$, ASTM 9-458, a high-temperature form of N), while at 1300°C it consists only of quartz ($d=3.43, 4.26, 1.817$, ASTM 33-1161).

The solubility in 2% citric acid solution of HAp calcined up to 1200°C is 41.0%. In the mixture calcined at 1100°C , the solubility of P_2O_5 is 94.6%. At 1300°C , the solubilities of both P_2O_5 and Na_2O reach 99.7% (Fig. 2-N). The content of the insoluble residue in the products calcined at temperatures above 1300°C is less than 1%.

Phase composition of calcined mixtures hydroxyapatite (HAp) + 20% silicate by X-ray diffraction data (soluble phases above and insoluble phases below the fraction line)

Mineral	Temperature, °C			
	1100	1200	1300	1400
Nepheline	$\beta\text{-Ca}_3(\text{PO}_4)_2$ (Na, K) AlSiO_4 (nepheline) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HAp) $\text{Ca}_2\text{Al}(\text{AlSiO}_7)$ (gehlenite)	$\beta\text{-Ca}_3(\text{PO}_4)_2$ $\text{Ca}_2\text{Al}(\text{AlSiO}_7)$ $\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$ (cornegicite)	$\alpha\text{-Ca}_3(\text{PO}_4)_2 \cdot 2\text{Ca}_2\text{SiO}_4$ (nagelschmidite) SiO_2 (quartz)	$\alpha\text{-Ca}_3(\text{PO}_4)_2 \cdot 2\text{Ca}_2\text{SiO}_4$ SiO_2
	Pseudolecite	$\beta\text{-Ca}_3(\text{PO}_4)_2$ KAlSi_3O_8 (orthoclase)	$\beta\text{-Ca}_3(\text{PO}_4)_2$ $\alpha\text{-Ca}_3(\text{PO}_4)_2 \cdot n\text{Ca}_2\text{SiO}_4$ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ KAlSi_2O_6 (leucite)	$\alpha\text{-Ca}_3(\text{PO}_4)_2 \cdot n\text{Ca}_2\text{SiO}_4$ KAlSi_2O_6
Glaucanite		$\beta\text{-}(\text{Ca}, \text{Mg})_3(\text{PO}_4)_2$ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ $\beta\text{-}(\text{Ca}, \text{Mg})_3(\text{PO}_4)_2$ Fe_2O_3 (magnetite) $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ (magnesioferrite) $(\text{Ca}, \text{Mg})\text{Si}_2\text{O}_6$ (diopside)	$\beta\text{-}(\text{Ca}, \text{Mg})_3(\text{PO}_4)_2$ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ $\beta\text{-}(\text{Ca}, \text{Mg})_3(\text{PO}_4)_2$ $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite) $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$ (andradite)	$\beta\text{-}(\text{Ca}, \text{Mg})_3(\text{PO}_4)_2$ $\beta\text{-}(\text{Ca}, \text{Mg})_3(\text{PO}_4)_2$ $\text{NaAlSi}_3\text{O}_8$ (albite) $(\text{Ca}, \text{Mg})\text{Si}_2\text{O}_6$ SiO_2 (quartz)
	Shungite	$\beta\text{-Ca}_3(\text{PO}_4)_2$ SiO_2 (quartz) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	$\beta\text{-Ca}_3(\text{PO}_4)_2$ SiO_2 (quartz, cristobalite) $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$ (akermanite)	$\alpha\text{-Ca}_3(\text{PO}_4)_2 \cdot n\text{Ca}_2\text{SiO}_4$ SiO_2 (cristobalite) $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$

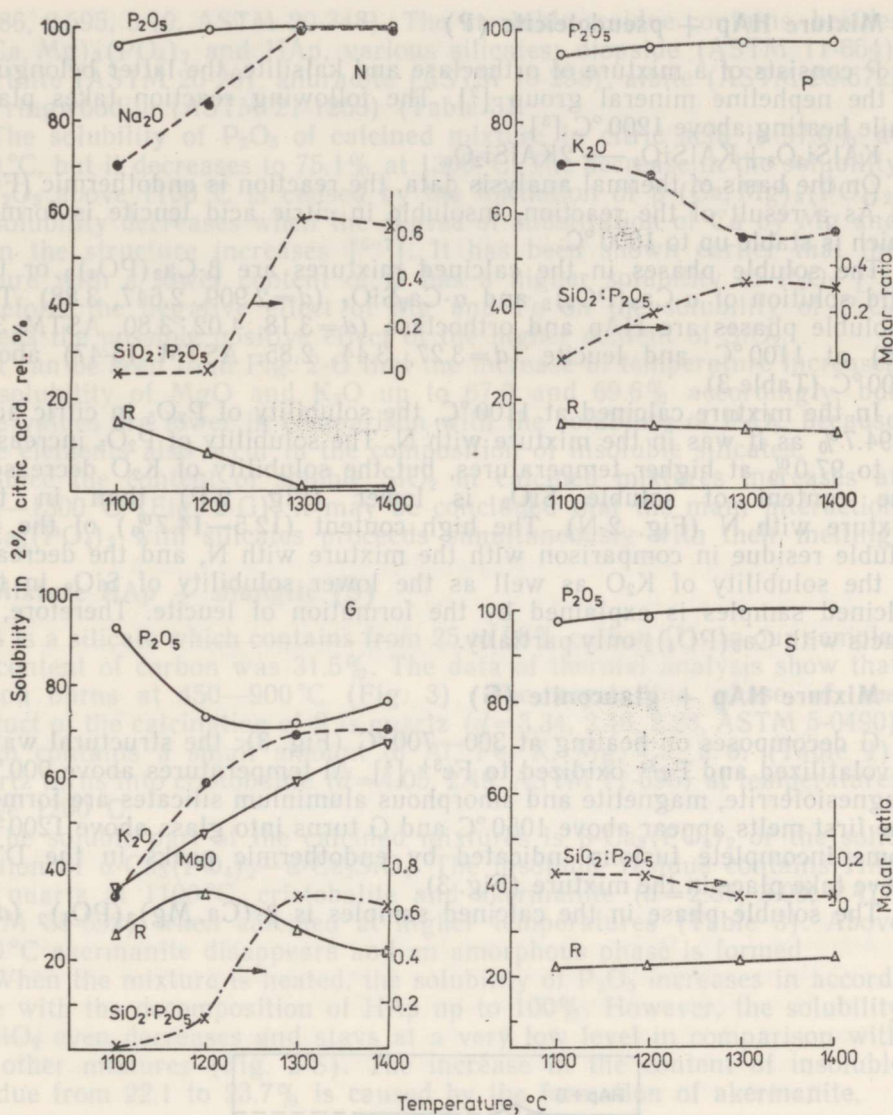
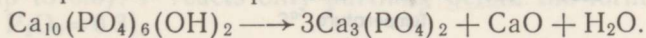


Fig. 2. Dependence of the solubility of calcined mixtures and of the molar ratio for soluble SiO_2 and P_2O_5 from temperature. N — nepheline, P — pseudoleicite, G — glaucinite, S — shungite; R — insoluble residue in 2% citric acid.

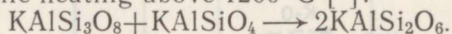
The increase in the solubility of calcined products is the result of the decomposition of HAp and the formation of $\beta-Ca_3(PO_4)_2$ and nagelschmidite. The nagelschmidite formation reaction takes place after the melting of N as is indicated by the increase in the content of soluble SiO_2 in the product of calcination above 1200°C (Fig. 2-N). Formation of gehlenite is due to the reaction of N with CaO formed as the result of the decomposition of HAp above 1000°C:



Aluminium silicates form an amorphous phase above 1200°C.

2. Mixture HAp + pseudoleucite (P)

P consists of a mixture of orthoclase and kalsilite, the latter belonging to the nepheline mineral group [2]. The following reaction takes place while heating above 1200 °C [3]:



On the basis of thermal analysis data, the reaction is endothermic (Fig. 1). As a result of the reaction, insoluble in citric acid leucite is formed which is stable up to 1600 °C.

The soluble phases in the calcined mixtures are $\beta\text{-Ca}_3(\text{PO}_4)_2$ or the solid solution of $\alpha\text{-Ca}_3(\text{PO}_4)_2$ and $\alpha\text{-Ca}_2\text{SiO}_4$ ($d=2.909, 2.647, 3.88$). The insoluble phases are HAp and orthoclase ($d=3.18, 4.02, 3.80$, ASTM 31-966) at 1100 °C, and leucite ($d=3.27, 3.44, 2.85$, ASTM 15-47) above 1200 °C (Table 3).

In the mixture calcined at 1100 °C, the solubility of P_2O_5 in citric acid is 94.7% as it was in the mixture with N. The solubility of P_2O_5 increases up to 97.0% at higher temperatures, but the solubility of K_2O decreases. The content of soluble SiO_2 is lower (Fig. 2-P) than in the mixture with N (Fig. 2-N). The high content (12.5–14.7%) of the insoluble residue in comparison with the mixture with N, and the decrease in the solubility of K_2O as well as the lower solubility of SiO_2 in the calcined samples is explained by the formation of leucite. Therefore, P reacts with $\text{Ca}_3(\text{PO}_4)_2$ only partially.

3. Mixture HAp + glauconite (G)

G decomposes on heating at 300–700 °C (Fig. 3): the structural water is volatilized and Fe^{2+} oxidized to Fe^{3+} [4]. At temperatures above 900 °C, magnesioferrite, magnetite and amorphous aluminium silicates are formed. The first melts appear above 1050 °C and G turns into glass above 1200 °C. Some incomplete fusions indicated by endothermic peaks in the DTA curve take place in the mixture (Fig. 3).

The soluble phase in the calcined samples is $\beta\text{-(Ca, Mg)}_3(\text{PO}_4)_2$ ($d=$

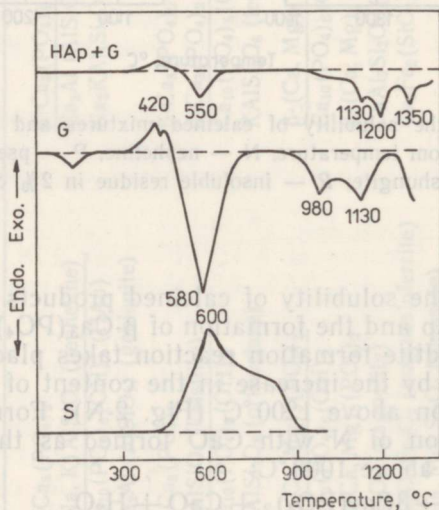


Fig. 3. DTA curves for glauconite (G) and shungite (S) and for the mixture of G with hydroxyapatite (HAp) in air with heating rate 10°/min (MOM instrument).

=2.86, 2.595, 3.19, ASTM 20-348). The insoluble residue contains, besides β -(Ca, Mg) $_3$ (PO $_4$) $_2$ and HAp, various silicates: diopside (ASTM 11-654), anorthite (ASTM 20-20), andradite (ASTM 10-238), albite (ASTM 20-572) and ringwoodite (ASTM 21-1258) (Table 3).

The solubility of P $_2$ O $_5$ of calcined mixture in citric acid is 97.0% at 1100°C, but it decreases to 75.1% at 1300°C. The decrease in the solubility of P $_2$ O $_5$ above 1100°C is caused by the formation of β -(Ca, Mg) $_3$ (PO $_4$) $_2$. Its solubility decreases when the degree of substitution of Ca by Mg and Fe in the structure increases [5-7]. It has been shown earlier that the mixture with a lower content of G has a higher solubility of P $_2$ O $_5$ [8]. Therefore, the negative effect of Mg and Fe on the solubility of P $_2$ O $_5$ exceeds the possible positive effect of the higher content of SiO $_2$.

It can be seen from Fig. 2-G that the increase in temperature increases the solubility of MgO and K $_2$ O up to 67.0 and 69.6% accordingly, but these values are lower in comparison with the solubility of P $_2$ O $_5$, because these elements also occur in the composition of insoluble silicates.

Since the content of soluble SiO $_2$ in calcined mixtures increases at 1200-1300°C (Fig. 2-G), it may be concluded that the main interaction of Ca $_3$ (PO $_4$) $_2$ with silicates proceeds simultaneously with their melting.

4. Mixture HAp + shungite (S)

S is a silicate which contains from 25 to 98% carbon [9]. In our sample, the content of carbon was 31.5%. The data of thermal analysis show that carbon burns at 450-900°C (Fig. 3). The crystalline phase of the product of the calcination of S is quartz ($d=3.34, 2.46, 2.28$, ASTM 5-0490) which contains a small amount of Al, Fe, K, Mg, Ca, a.o. (Table 1). Quartz turns into cristobalite ($d=4.05, 2.49$, ASTM 11-695) at temperatures above 1200°C.

The soluble part of the calcined mixtures is β -Ca $_3$ (PO $_4$) $_2$ or the solid solution of α -Ca $_3$ (PO $_4$) $_2$ - α -Ca $_2$ SiO $_4$. The insoluble residue contains HAp and quartz at 1100°C, cristobalite and akermanite ($d=2.87, 3.09, 2.477$, ASTM 35-592) when calcined at higher temperatures (Table 3). Above 1300°C akermanite disappears and an amorphous phase is formed.

When the mixture is heated, the solubility of P $_2$ O $_5$ increases in accordance with the decomposition of HAp up to 100%. However, the solubility of SiO $_2$ even decreases and stays at a very low level in comparison with the other mixtures (Fig. 2-S). The increase in the content of insoluble residue from 22.1 to 23.7% is caused by the formation of akermanite.

CONCLUSIONS

The decomposition of HAp on heating is enhanced in the mixtures with silicates. The composition and properties of the calcination products depend on the chemical composition, as well as on the mineral composition of silicates. CaO formed as the result of the decomposition of HAp connects with silicates forming gehlenite in the mixture with N, diopside, anorthite and andradite are formed in the mixture with G, and akermanite in the mixture with S and α -Ca $_2$ SiO $_4$. The formation reactions of solid solutions of calcium phosphate and silicate take place mainly at temperatures above 1200°C. If the silicate melts (N, G), there is a high content of soluble in citric acid SiO $_2$ in the product (the molar ratio of soluble SiO $_2$:P $_2$ O $_5$ is up to 0.6). P reacts only partially before the formation of leucite (SiO $_2$:P $_2$ O $_5=0.3$).

The soluble in citric acid crystalline phases in the products of calcination are α -Ca $_3$ (PO $_4$) $_2$ and its solid solutions with α -Ca $_2$ SiO $_4$, nagelschmidite, and phases based on β -Ca $_3$ (PO $_4$) $_2$.

The most negative effect on the solubility of P_2O_5 is caused by Mg and Fe. Besides, it is not compensated even by higher content of SiO_2 in the mixture.

Leucite and quartz (cristobalite) do not react with $Ca_3(PO_4)_2$ at temperatures up to $1400^\circ C$.

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TERMOKEEMILISED REAKTSIOONID SÜSTEEMIDES HÜDROKSIIDAPATIIT—ALUMOSILIKAAT VÕI ŠUNGIIT

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Hüdroksiidapatiidi ja alumosilikaadi (nefeliin, pseudoleutsiit, glaukoniit) või šungiidi segude kuumutamisel 1400°C-ni toimuvaid reaktsioone uuriti termilise, keemilise ja röntgendifraktsioonanalüüsi meetoditega. Segudes silikaatidega kiireneb kuumutamisel hüdroksiidapatiidi lagunemine. Nefeliin ja glaukoniit reageerivad $\text{Ca}_3(\text{PO}_4)_2$ -ga peaaegu täielikult, pseudoleutsiit reageerib osaliselt enne üleminekut leutsiidiks. Šungiidi kuumutussaadus (kvarts, kristobaliit) ei reageeri $\text{Ca}_3(\text{PO}_4)_2$ -ga temperatuuril kuni 1400°C. Sidrunhappe kaheprotsendises lahuses lahustuvad kuumutusproduktide kristalsed faasid on $\alpha\text{-Ca}_3(\text{PO}_4)_2$ ja selle tahked lahused $\alpha\text{-Ca}_2\text{SiO}_4$ -ga, nagelschmidtitiit ja faasid $\beta\text{-Ca}_3(\text{PO}_4)_2$ alusel.

ТЕРМОХИМИЧЕСКИЕ РЕАКЦИИ В СИСТЕМАХ ГИДРОКСИДАПАТИТ—АЛЮМОСИЛИКАТ ИЛИ ШУНГИТ

Кайя ТЫНСУААДУ, Карел РИММ

Термическим, рентгендифракционным и химическим методами анализа изучены реакции, протекающие в смесях гидроксидапатита с алюмосиликатами (нефелином, псевдолейцитом, глауконитом) или с шунгитом (кварцем, кристобалитом) при их прокаливании до 1400°C. Установлено, что при прокаливании смесей разложение гидроксидапатита ускоряется. Непелин и глауконит реагируют с $\text{Ca}_3(\text{PO}_4)_2$ почти полностью, псевдолейцит реагирует частично до превращения его в лейцит. Продукты прокаливании шунгита не взаимодействуют с $\text{Ca}_3(\text{PO}_4)_2$ до температуры 1400°C. Кристаллическими фазами, растворимыми в 2%-ном растворе лимонной кислоты, являются $\alpha\text{-Ca}_3(\text{PO}_4)_2$, его твердые растворы с $\alpha\text{-Ca}_2\text{SiO}_4$, нагельшмидтит и фазы на основе $\beta\text{-Ca}_3(\text{PO}_4)_2$.