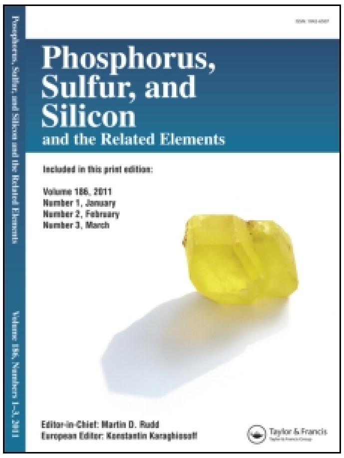

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THERMAL REACTIONS IN SYNTHETIC APATITE–AMMONIUM SULFATE MIXTURE

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The thermal reactions in the mixtures of hydroxylapatite or fluorapatite and $(NH_4)_2SO_4$ up to 500°C were studied with the purpose of elaborating the conditions of obtaining calcium–ammonium cyclophosphate that could be used as fertilizer. Thermal analysis with a simultaneous FTIR analysis of the evolved gases as well as the analyses of chemical and phase composition of solid products were performed. The thermal changes in the mixtures could be divided into three steps: (1) decomposition of $(NH_4)_2SO_4$ and reactions of apatite with these products at 250–420°C, (2) calcium ammonium polyphosphate formation at 290–450°C, and (3) reaction of $CaSO_4$ with $CaNH_4P_3O_9$ at 320–500°C. Higher concentrations of NH_3 in the gas phase promote the formation of $CaNH_4P_3O_9$ and increase its stability. Calcination at temperatures above 350°C causes decomposition of $CaNH_4P_3O_9$ with a decrease in the content of water-soluble phosphorus and evolvement of SO_2.

Keywords: Ammonium sulfate; calcium–ammonium cyclophosphate; evolved gases; fluorapatite; hydroxylapatite; thermal reactions

INTRODUCTION

Different methods and reactions of apatite decomposition for fertilizer production are in use, but they all need a lot of energy or water.[1] Thermal reactions in mixtures of natural apatite and ammonium sulfates were studied since the early 1960s in the USSR, France, and Bulgaria,

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with the aim of obtaining nitrogen–phosphorus fertilizers. The problem of utilizing large amounts of $(NH_4)_2SO_4$ as a by-product of chemical industry has called attention to this problem again.[2,3]

A reaction (Equation (1)) between apatite and ammonium sulfate with $CaNH_4P_3O_9$ formation at temperatures up to 450°C was reported by Welch[4]—a reaction for obtaining a water-soluble polyphosphate:

$$\begin{aligned} Ca_5(PO_4)_3F + 4(NH_4)_2SO_4 \rightarrow CaNH_4P_3O_9 + CaSO_4 + NH_4F \uparrow \\ + 6NH_3 \uparrow + 3H_2O \uparrow \end{aligned} \tag{1}$$

In the study of the calcination, up to 500°C of hydroxylapatite–ammonium sulfate mixtures, formation of $Ca_2(NH_4)_2(SO_4)_3$, di-, tri- and other polyphosphates, and $CaSO_4$ was observed.[5]

The synthesis of calcium-ammonium-tricyclophosphate using other calcium phosphates, mainly calcium dihydrogenphosphate, revealed that its formation occurs in the temperature interval of 300–350°C.[6–9] At temperatures above 360°C, decomposition of $CaNH_4P_3O_9$[4,6,7,9] and, in some studies, release of sulfur oxides[7] and loss of phosphorus[4] from apatite–ammonium sulfate mixture was reported. To sum up, the conditions of obtaining $CaNH_4P_3O_9$ from apatite are not established in detail and need specification.

The aim of the study was to elucidate the reactions taking place in the mixture of apatite and $(NH_4)_2SO_4$ at heating up to 500°C and the conditions of formation of $CaNH_4P_3O_9$. Particular attention was paid to the evolving mixtures of gases.

MATERIALS AND METHODS

In preparation of apatite–$(NH_4)_2SO_4$ mixtures synthetic apatites were used. Hydroxylapatite (HAp; CaO, 48.42%; P_2O_5, 41.41%; H_2O, 5.93%) was a biochemical of "Fluka" for chromatography. Fluorapatite (FAp; CaO, 55.43%; P_2O_5, 41.15%; F, 3.00%) was synthesized by thermal reaction of $CaHPO_4 \cdot 2H_2O$ and CaF_2 mixed in proportion according to stoichiometry of FAp and calcined at first at 1000°C during 5 h, grained and newly calcined at 1100°C for 3 h, and analyzed by XRD. The $(NH_4)_2SO_4$ used was a chemical pure grade (NH_3, 25.76; SO_3, 60.61%). The mole ratio in the apatite–$(NH_4)_2SO_4$ mixtures was 1:4 according to the reaction in Equation (1). The mixtures of apatite and $(NH_4)_2SO_4$ were ground in an agathe ball mill for 30 min.

For thermal analysis a Derivatograph (MOM-Q1000, Hungary) and a Setaram LabSys 2000 were used. The experiments with MOM

Derivatograph were carried out in a static air atmosphere in a multiplate and labyrinth-type Pt sample holder. The thickness of the sample layer in the plate crucible was about 1 mm, and the sample mass was 300–500 mg. The heating rate was 5°C/min. A thermal analysis with the Setaram instrument was carried out at heating rate of 10°C/min in an air flow of 50 ml/min in open Pt crucible, sample mass ~30 mg. On-line gas composition was monitored using Fourier transform infrared (FTIR) gas analyzer (Interspectrum). The Ranger-AlP Gas cell S/N 23790 (Reflex Analytical Co.) with 8.8 m path length was maintained at 150°C. Spectra were recorded in the 600–4000 cm^{-1} region with a resolution of 4 cm^{-1} and 4 scans per slice.

The samples (500 mg) for chemical, infrared (IR), and X-ray diffraction (XRD) analyses were calcined in open crucibles up to a chosen temperature and were held at that temperature until the mass change stopped, up to 2–4 h, at MOM Derivatograph. The XRD analysis was carried out with a DRON-4 diffractometer ($2\Theta = 8$–60°, step size 0.04°). IR spectra were obtained on an Interspectrum 2000 FTIR spectrometer in the range of 400–4000 cm^{-1} using KBr pellets (300 mg KBr/1 mg sample).

The chemical composition of the starting materials as well as that of the products of calcination was determined by standard analytical methods: phosphorus spectrophotometrically as phosphomolybdate yellow complex; fluorine potentiometrically with Fluoride COMB.ISE/BNC fluorselective electrode; calcium titrimetrically after precipitation in oxalate form; sulfur gravimetrically in the form of $BaSO_4$; NH_3 by Kjeldahl method.

RESULTS

Thermal Analysis

The thermogravimetric (TG) and differential thermal analysis (DTA) curves of HAp, $(NH_4)_2SO_4$ and its mixtures with HAp and FAp in different gas diffusion conditions are given in Figures 1 and 2. No thermal effect occurs in FAp up to 500°C. A mass loss in HAp in the temperature interval 200–450°C is due to the loss of structural water.[10] $(NH_4)_2SO_4$ decomposition can be divided by the mass loss mainly into two steps. The first step was assigned to the loss of NH_3 and the second one to the decomposition of the $(NH_4)HSO_4$ or H_2SO_4 formed, with release of NH_3, SO_2, and H_2O.[11,12]

Thermal changes in the mixtures of $(NH_4)_2SO_4$ with HAp and FAp do not differ remarkably. The mass loss occurs in 2–3 steps. The first step culminates in both cases at 290°C and the second one at 360 and

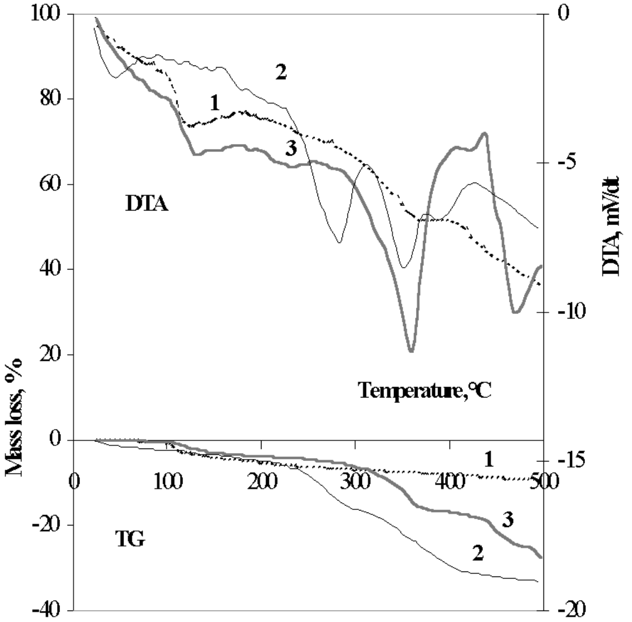

FIGURE 1 TG and DTA curves of hydroxylapatite and its mixture with $(NH_4)_2SO_4$. Heating rate 5°C/min, in stationary air. 1, hydroxylapatite; 2, HAp + $(NH_4)_2SO_4$ in multiplate crucible; 3, HAp + $(NH_4)_2SO_4$ in labyrinth crucible.

380°C in the mixtures with HAp and FAp, respectively, in multiplate crucible. In the labyrinth crucible the temperatures of the maximum are higher by 80–90°C. Therefore the temperatures of the endothermic reactions depend on the type of crucible used, more specifically on the conditions of removal of the arising gases. In case of a labyrinth crucible the pressure of the evolving gases may be higher by about 100 kPa.[13] The final mass loss in both crucibles is equal to that of FAp. In the mixture of HAp the mass loss in plate crucible exceeds the mass loss in labyrinth crucible by 5.7%. The temperature of the first step is almost the same as for $(NH_4)_2SO_4$, but the mass loss is up to twice as large in the mixtures. The second major effect in the mixtures lies at about 40–50°C higher temperature in comparison with pure $(NH_4)_2SO_4$.

FTIR Analysis of the Gases Evolved

The gases evolved were identified using characteristic infrared absorption wavelengths: for NH_3 at 930 and 963 cm^{-1}, SO_2 at 1345 and 1378 cm^{-1}, H_2O 1520, 1700, and 3855 cm^{-1}, N_xO_y at 2358

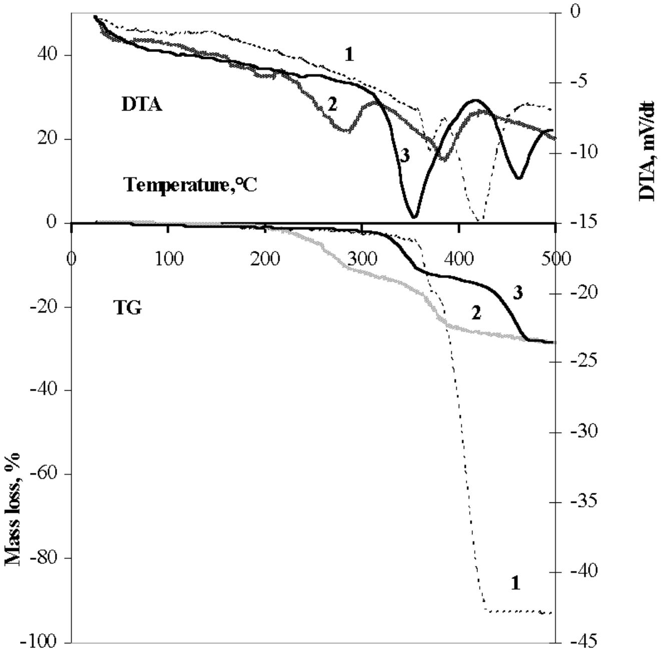

FIGURE 2 TG and DTA curves of $(NH_4)_2SO_4$ and its mixture with fluorapatite. Heating rate 5°C/min, in stationary air. 1, $(NH_4)_2SO_4$; 2, FAp + $(NH_4)_2SO_4$ in multiplate crucible; 3, FAp + $(NH_4)_2SO_4$ in labyrinth crucible.

and 2242 cm^{-1}.[14] The profiles of evolvement of gases, presented in Figures 3–5, were obtained as temperature derivatives of the peak area integrated above baseline from 900 to 980 cm^{-1} for NH_3, from 1285 to 1410 cm^{-1} for SO_2, and from 2138 to 2274 cm^{-1} for N_xO_y. H_2O spectrum is masked by NH_3 spectra. Gaseous HF was not identified because of the lack of IR spectral information. Condensation of NH_4F in a cooler part of the furnace (~150°C) of the thermal analyzer could also take place.

Due to the higher sensitivity of Setaram equipment used in gas analysis experiments it was established that the decomposition of $(NH_4)_2SO_4$ takes place as a result of four overlapping reactions (Figure 3) in the air flow: DTG peaks at 327, 343, 392, and 423°C. Decomposition starts at 250°C with release of NH_3, while above 320°C SO_2 evolves, in agreement with the results of the earlier studies.[11] The presence of nitrogen oxides in the gas phase is explained by the secondary oxidation of NH_3 catalyzed by Pt (crucible). When a corundum crucible was used no nitrogen oxides were detected.

The study of the gases evolved from the apatite–$(NH_4)_2SO_4$ mixtures shows that the first step in mass loss in the temperature interval

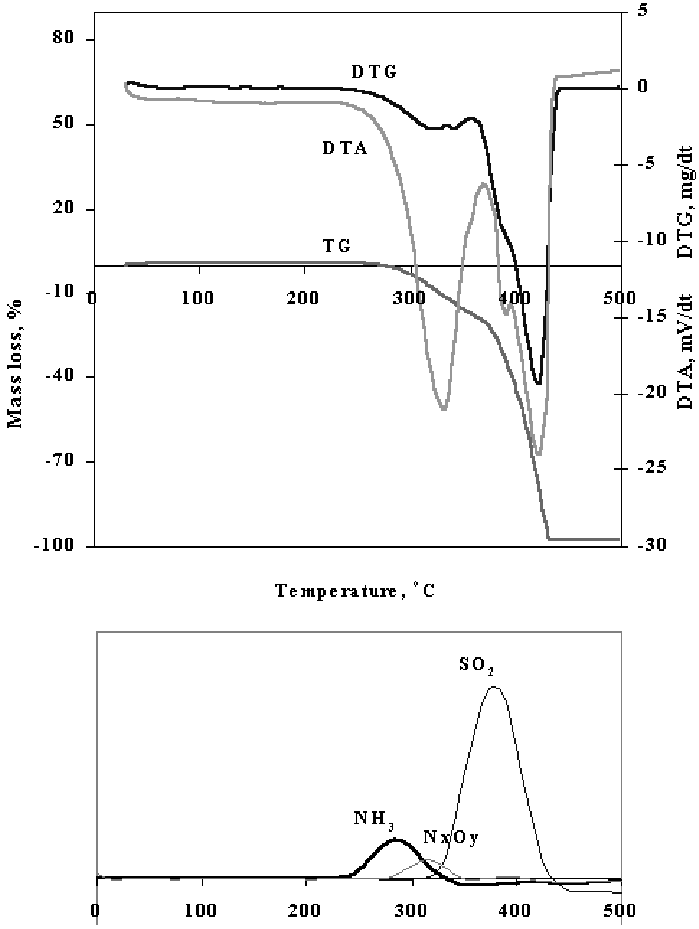

FIGURE 3 TG, DTG, and DTA curves of $(NH_4)_2SO_4$ and profiles of the evolved gases. Heating rate 10°C/min, in the air flow 50 ml/min.

from 210–230°C to 350–360°C corresponds to the release of NH_3. The subsequent production of nitrogen oxides in the mixture with FAp (Figures 4 and 5) suggests some possible cocatalyzing effect of HF in the oxidation of NH_3.

During the second mass loss step in the temperature interval from 350–360°C to 430–435°C, mainly SO_2 evolves. In the interval a slight wave of nitrogen oxides or NH_3 is observed. NH_3 could disappear from the gas phase at temperatures above 350°C as a result of the reaction with SO_3 and condensation of $(NH_4)_2SO_4$ in a cooler part of the furnace.

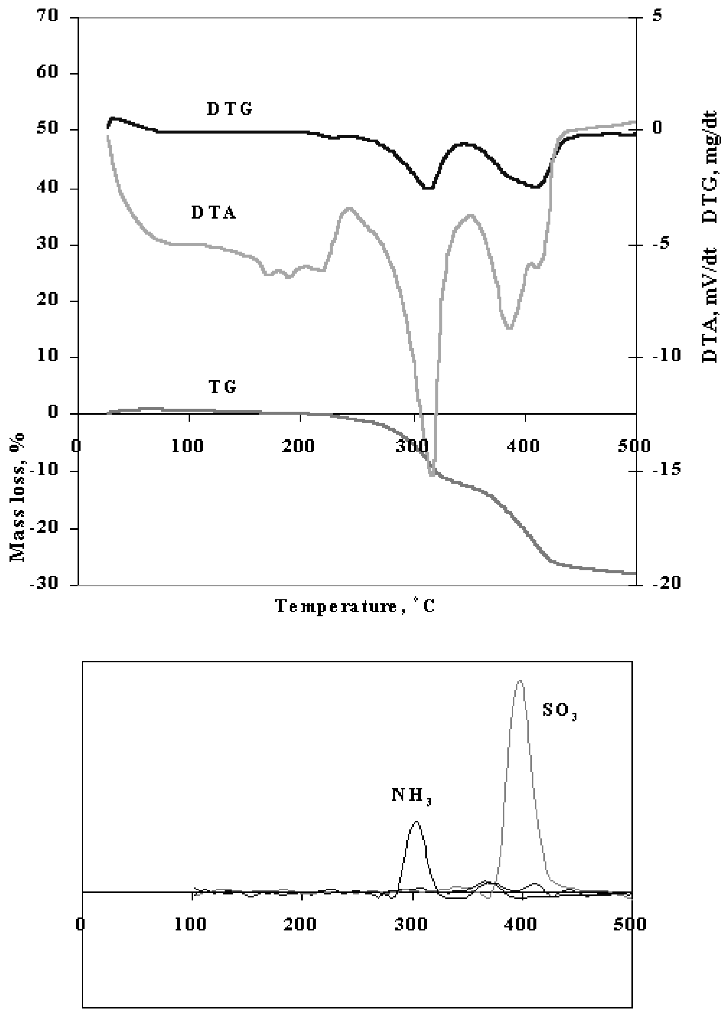

FIGURE 4 TG, DTG, and DTA curves of HAp + $(NH_4)_2SO_4$ mixture and profiles of the evolved gases. Heating rate 10°C/min, in the air flow 50 ml/min.

Solid Phase Analysis

The chemical and phase composition of solid products of calcination of the mixtures up to constant mass at 270, 330, and 500°C are given in Table I. The chemical analysis confirmed that 85% of fluorine and 52% of NH_3 is lost due to the reactions at temperatures up to 270°C. From the total amount of sulfur, 8.6 and 10.4% is lost in the mixtures with HAp and FAp, respectively, on calcination at 330°C and 18.0% at 500°C.

TABLE I Chemical and Phase Composition of $(NH_4)_2SO_4$–Apatite Mixtures

Sample	HAp + $(NH_4)_2SO_4$				FAp + $(NH_4)_2SO_4$			
Temperature, °C	20	270	330	500	20	270	330	500
Mass loss,%	0	16	27	35	0	11	25	29
CaO, %	22.31	26.56	30.57	34.33	25.54	28.79	34.06	35.96
P_2O_5, %	19.08	22.72	26.14	29.36	18.96	21.37	25.28	27.34
SO_3, %	32.68	38.9	37.93	36.17	32.68	36.72	36.62	34.46
F, %	0	0	0	0	1.38	0.21	0.08	0.10
NH_3, %	13.89	7.6	1.92	0.09	13.89	7.44	2.10	0.93
Water soluble								
P_2O_5, %		16.5	24.3	11.2		14.5	22.8	17.8
P_2O_5 rel., %		72.6	93.0	38.2		62.1	90.2	65.1
Phase composition by XRD and IR	HAp $(NH_4)_2SO_4$	$Ca_2(NH_4)_2(SO_4)_3$ HAp $[Ca(PO_3)_2]_n$	$CaNH_4P_3O_9$ $CaSO_4$	$CaSO_4$ $[Ca(PO_3)_2]_n$	FAp $(NH_4)_2SO_4$	$Ca_2(NH_4)_2(SO_4)_3$ FAp $[Ca(PO_3)_2]_n$	$CaNH_4P_3O_9$ $CaSO_4$	$CaSO_4$ $[Ca(PO_3)_2]_n$ $CaNH_4P_3O_9$

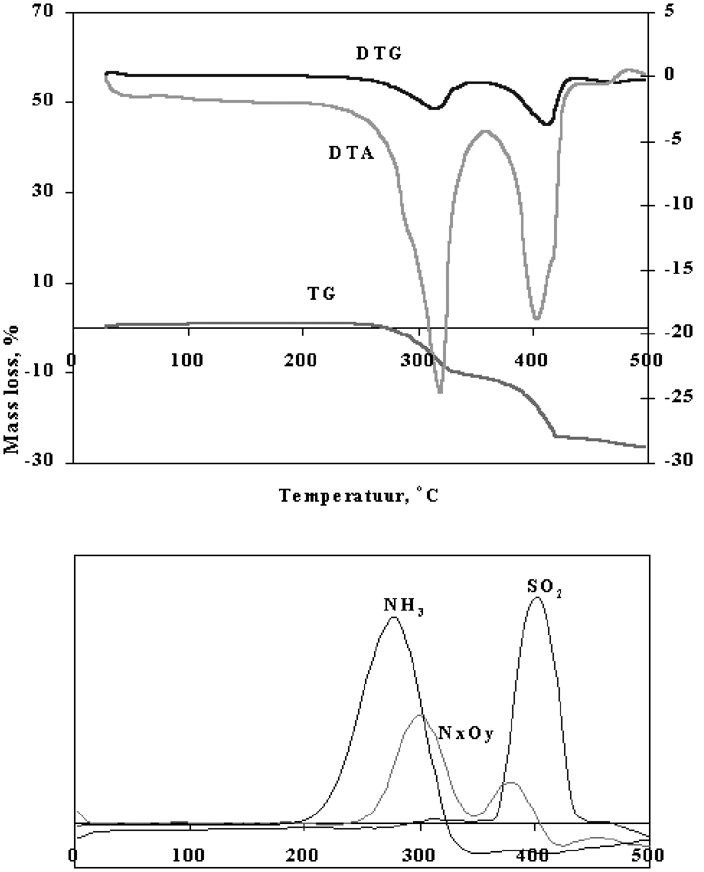

FIGURE 5 TG, DTG, and DTA curves of FAp + $(NH_4)_2SO_4$ mixture and profiles of the evolved gases. Heating rate 10°C/min, in the air flow 50 ml/min.

The content of water-soluble phosphorus is the highest at 330°C, up to 90–93 rel.%.

The analysis of XRD spectra (see Figure 6 for the FAp–$(NH_4)_2SO_4$ system) revealed that the main crystalline phase at 270°C is $Ca_2(NH_4)_2(SO_4)_3$ (JCPDS Card No. 22–1037, d = 3.334, 4.30, 2.815 Å).[15] The content of apatite in these samples is strongly reduced. In the samples calcined at 330°C, the presence of $CaNH_4P_3O_9$ (JCPDS Card o. 21-0792, d = 5.38, 5.01, 5.28 Å) and $CaSO_4$ (JCPDS Card No. 37-1496, d = 3.499, 2.849, 2.328 Å) was established. In the solid products of calcination in open crucibles up to 500°C the only crystalline phase determined was $CaSO_4$ or γ-$CaSO_4$, in labyrinth crucibles very weak peaks of $CaNH_4P_3O_9$ were also found.

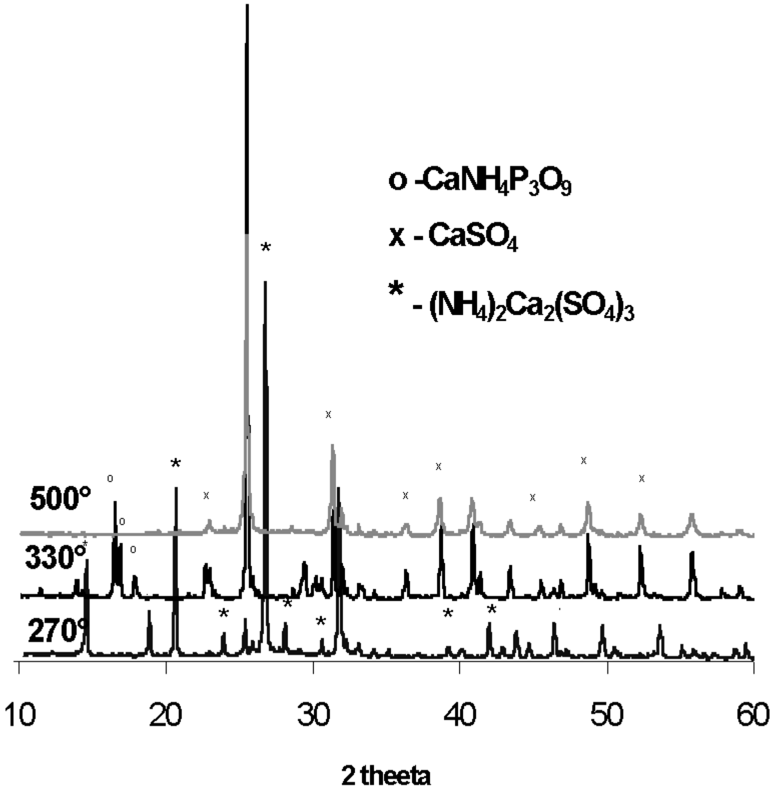

FIGURE 6 XRD spectra of products of calcination of FAp + $(NH_4)_2SO_4$ mixture.

The results of FTIR spectroscopic analysis of the products of calcination confirmed the results of XRD analysis and allowed the establishment of the form of amorphous phosphate compounds. In accordance with the decrease in NH_3 content in the samples at calcination the intensity of a peak characteristic for NH_4 group at 1431 cm^{-1} (see Figure 7 for the HAp-$(NH_4)_2$ SO_4 system) decreases. The positions of SO_4 absorption bands shift from 646 and 613–617 cm^{-1} to 676 and 596 cm^{-1}, when $Ca_2(NH_4)_2(SO_4)_3$ decomposes and $CaSO_4$ appears.[16] The spectra of the products of calcination at 330°C exhibit ν_s strong peaks of P—O—P at 782 and 1006 cm^{-1}, ν_{as} of PO_2 at 1277–1315, and δ P—O at 506 cm^{-1}, which are characteristic of cyclophosphates.[17] In the spectra of the products of calcination at 270 and 500°C the ν_{as} bands of PO_2 at 1270–1320, ν_{as} of P—O—P at 902–905, and δ P—O at 530–480 cm^{-1} can be assigned to calcium polyphosphate.[17]

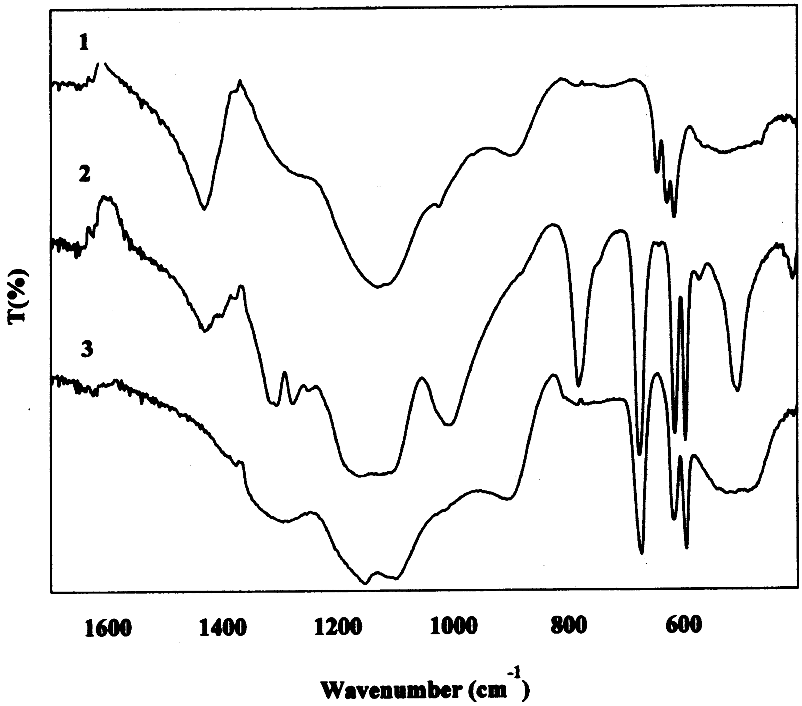

FIGURE 7 FTIR spctra of products of calcination of HAp + $(NH_4)_2SO_4$ mixture. 1, 270°C; 2, 330°C; 3, 550°C.

DISCUSSION

It was found that, after $(NH_4)_2SO_4$ decomposition, starting at 220°C, by the reactions in Equations (2) and (3),[11]

$$(NH_4)_2SO_4 \rightarrow NH_3 \uparrow + NH_4HSO_4 \quad (2) \quad \text{and} \quad NH_4HSO_4 \rightarrow H_2SO_4 + NH_3 \uparrow \qquad (2)$$

in the mixture of $(NH_4)_2SO_4$ with apatite, the reaction between apatite and the products of decomposition of $(NH_4)_2SO_4$ takes place as indicated by the additional volatilization of NH_3 and H_2O in comparison with pure $(NH_4)_2SO_4$ and a decrease in the fluorine content in the solid phase (Table I). Below 300°C several reactions could occur simultaneously, resulting in NH_3 and HF and/or H_2O release and formation of calcium polyphosphate, conventionally formulated as $[Ca(PO_3)_2]_n$, together with $Ca_2(NH_4)_2(SO_4)_3$or $CaSO_4$.

$$Ca_5(PO_4)_3F + 5.25NH_4HSO_4 \rightarrow 1.75Ca_2(NH_4)_2(SO_4)_3 + 1.5Ca(PO_3)_2 + HF\uparrow + 1.75NH_3\uparrow + 3H_2O\uparrow \quad (3)$$

$$Ca_5(PO_4)_3F + 3.5NH_4HSO_4 \rightarrow 3.5CaSO_4 + 1.5Ca(PO_3)_2 + HF\uparrow + 3.5NH_3\uparrow + 3H_2O\uparrow \quad (4)$$

In conditions of relatively high partial pressures of ammonia (labyrinth crucible), the reaction in Equation (3) should dominate; the increased yield of $Ca_2(NH_4)_2(SO_4)_3$ is expected to favor $CaNH_4P_3O_9$ formation by the reaction in Equation (5) in the temperature interval of 300–350°C.

$$Ca_2(NH_4)_2(SO_4)_3 + 3Ca(PO_3)_2 \rightarrow 3CaSO_4 + 2CaNH_4P_3O_9 \quad (5)$$

As a result, water-soluble phosphate is obtained. $Ca_2(NH_4)_2(SO_4)_3$ could also decompose by the reaction in Equation (6) as the content of sulfur decreases in the solid phase already at temperatures below 300°C.

$$Ca_2(NH_4)_2(SO_4)_3 \rightarrow 2CaSO_4 + 2NH_3\uparrow + SO_3\uparrow + H_2O\uparrow \quad (6)$$

Local decrease in the temperature in the gas phase may cause condensation of $(NH_4)_2SO_4$to take place Equation (7),

$$2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4 \quad (7)$$

altering the results of the analysis of gases. Decomposition of $CaNH_4P_3O_9$ with release of NH_3 causes ultraphosphates (Ca/P mole ratio is less than 0.5) reaction with $CaSO_4$ and formation of $[Ca(PO_3)_2]_n$ and SO_3 expressed by the reaction in Equation (8) at temperatures above 350°C, as also suggested by a decrease in the water-soluble phosphate and sulfur content:

$$2CaNH_4P_3O_9 + CaSO_4 \rightarrow 3Ca(PO_3)_2 + SO_3\uparrow + 2NH_3\uparrow + H_2O\uparrow \quad (8)$$

Contrary to the results obtained by Welch,[4] loss of phosphorus by possible reaction (Equation (9)) was not established, which can be explained with the shorter time of reaction.

$$2CaNH_4P_3O_9 \rightarrow 2Ca(PO_3)_2 + 2NH_3\uparrow + H_2O\uparrow + P_2O_5\uparrow \quad (9)$$

The actual temperatures of the reactions depend on the partial pressure of the evolved components, particularly on the ammonia content, as shown in the thermal analysis experiments.

CONCLUSIONS

The thermal reactions in the mixtures of hydroxylapatite (HAp) or fluorapatite (FAp) and $(NH_4)_2SO_4$ up to 500°C were studied by thermal analysis with a simultaneous analysis of the evolved gases as well as by the analyses of solid products.

The thermal changes in the mixtures could be divided into three steps: (1) decomposition of $(NH_4)_2SO_4$ and the reactions of apatite with these products at 250–420°C, (2) calcium ammonium polyphosphate formation at 290–450°C, and (3) decomposition of $CaNH_4P_3O_9$ and the following reactions with SO_3 release at 320–500°C. The composition of the solid products is very sensitive to the conditions of evolvement of the gases. A higher concentration of NH_3 in the gas phase promotes the formation of $CaNH_4P_3O_9$[4] and increases its stability. Calcination above 350°C causes decomposition of $CaNH_4P_3O_9$, together with a decrease in the content of water-soluble phosphorus and release of NH_3 and SO_3.

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