

THERMOCHEMICAL INVESTIGATIONS OF NATURAL PHOSPHATE WITH AMMONIUM SULPHATE ADDITIVE

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The free energy of the acidic ammonium sulphate is a good precondition its use as an additive or reagent for decomposition of natural phosphates on the way to obtain NPS or NPKS complex fertilizers. During our previous studies it was confirmed that as a result of thermo-mechanical treatment new solid phases are formed as a result of the phosphates decomposition.

The aim of this study is to find out appropriate conditions for thermal treatment of Tunisia phosphorite with ammonium sulphate where the content of P₂O₅ soluble forms has its maximum. The process was investigated under dynamic thermal conditions. Structure and phase transformations of the mixtures to intermediate and final solid products are confirmed by different techniques. X-ray powder diffraction, infrared spectroscopy and electron microscopy have been applied successfully and relationship found between phase structure and thermal treatment applied. As a result of the complex studies optimal temperatures are determined. The solid products under optimal conditions contain phosphorous in soluble forms available for plants in the soil. As a final it is concluded that the final products could be used as complex mineral fertilizers.

Keywords: ammonium sulphate, calcium ammonium polyphosphates, released gases, solid phases, thermal decomposition, Tunisian phosphate

Introduction

Ammonium sulphate is a by-product of various industrial production processes such as caprolactam and methyl methacrylate but a trend exists for its growth resulting from the commissioning of various plants for treatment of coke oven gases and waste gases from thermal power plants [1]. This increases the interest in using ammonium sulphate as a reagent in processing of natural phosphates to new NPS and NPKS complex fertilizers. Various researchers [2–15] have studied thermal behaviour of phosphates and ammonium sulphate. At temperatures 773 K are identified Ca(H₂PO₄)₂, CaHPO₄, CaH₂P₂O₇, NH₄CaP₃O₉, CaSO₄ [6, 8, 10, 11], and at 1273 K α,β-Ca₃(PO₄)₂, β-Ca(PO₃)₂, α,β-Ca₂P₂O₇, [6, 8, 10, 12, 13]. Some authors [6, 10, 14] consider formation of CaNH₄P₃O₉ as an important stage in the diagram of possible chemical interactions. The authors suggest different chemical reactions producing ortho-, pyro- and polyphosphates, as well as further transformations at higher temperatures [2–14]. There is a limited data about emitted gaseous components [5].

The aim of this paper is to study the intermediates and end products after thermal treatment of Tunisia phosphorite (TF) and ammonium sulphate (AS) mixtures under dynamic and isothermal heating up

to 1273 K in an air gas environment. The use of thermodynamic, thermal and spectroscopy methods for analyses and analysis of released gases aims to establish the temperature and phase transformations during thermal treatment of Tunisia phosphorite – ammonium sulphate mixtures.

Experimental

Materials and methods

Tunisia phosphorite contain (mass%): 29.58P₂O₅, 48.40CaO, 6.48CO₂, 3.58SO₃, 1.88SiO₂, 2.74F, 1.38Na₂O, 0.07K₂O, 0.056Cl. AS is a by-product from the electron-beam waste gas cleaning system in the Thermal Power Plant Maritsa-East-2 that contains 99.2% AS. ‘Stanton Redcroft’ and ‘Setaram’ are the thermoanalysers. The studies, conducted under a dynamic heating regime involved samples weighing 15.20±0.4 mg, within a temperature range of 298–1273 K, heating rate 10 K min⁻¹ and air flow-rate 50 mL min⁻¹. A thermal analysis coupled with evolved gas phase analysis was carried out at 10 K min⁻¹ heating rate and 50 mL min⁻¹ air flow in open corundum crucible; sample mass ~20 mg and the Setaram LabSys 2000 instrument used. On-line

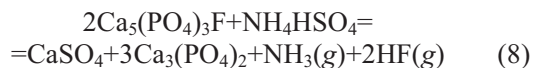
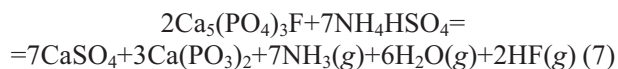
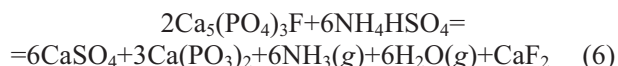
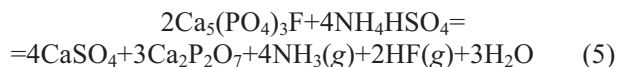
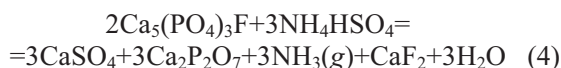
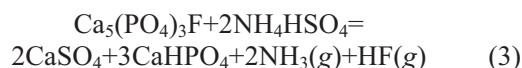
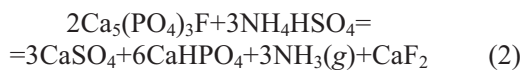
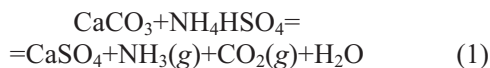
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gas composition was monitored using FTIR gas analyser (Interspectrum). The Ranger-ALP Gas cell S/N 23790 (Reflex Analytical Co.) with 8.8 m path length was maintained at 423 K. Spectra were recorded in the 600–4000 cm^{-1} region with a resolution of 4 cm^{-1} and 4 scans per slice. The released gases 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 at 1520, 1700 and 3855 cm^{-1} , N_xO_y at 2358 and 2242 cm^{-1} , CO_2 at 2348, 2360 and 670 cm^{-1} . The profiles of the gas emissions were obtained as temperature derivatives of the peak area integrated above baseline from 900 to 983 cm^{-1} for NH_3 , from 1309 to 1400 cm^{-1} for SO_2 , from 2260 to 2405 cm^{-1} for CO_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 (~423 K) of the thermal analyzer could also take place. The studies conducted in isothermal heating conditions involved ceramic crucibles with sample mass of 200 mg. X-ray powder diffraction analyses were conducted using a DRON diffractometer, with $\text{CuK}\alpha$ radiation. The analysis was conducted by comparing experimental spectrums with the JCPDS database (JCPDS, Powder Diffraction File (PDF), Set 1(89, Joint Committee on Diffraction Standards, Philadelphia PA, 2001). The infrared spectrums of the samples were established on a Spekord M-80 made by Carl Zeiss Jena in an interval of 650–4600 cm^{-1} . The sample surfaces were observed using a scanning electronic microscope PHILIPS PH, model SEM 515 in a regime of secondary electronic emission (SE). The thermodynamic calculations were performed with HSC Chemistry 4, Outokumpu program. The mass ratio between two components is 1:1.

Results

Thermodynamic analysis

Thermodynamic calculations and reactions (1)–(8) were performed to determine the values of Gibbs energy (ΔG). The results obtained are shown in Fig. 1.



The thermodynamic analysis showed the possibility of reactions forming hydrogen ortho- and pyro-phosphates when heated to 773 K. There is an interesting higher probability of formation of $\text{Ca}(\text{PO}_3)_2$ (reactions (5) and (6)) at temperatures as high as 773 K, but not of $\text{Ca}_3(\text{PO}_4)_2$ (reaction (8)). Reaction (8) is possible at higher temperatures.

Thermal analysis of a TF and AS mixture, 1:1 under a dynamic heating regime

TG, DTG and DTA-data are presented in Fig. 2 and Table 1.

Table 1 Mass loss during thermal treatment under dynamic heating up to 1273 K ('Stanton Redcroft') of TF+AS (mass ratio=1:1)

No.	Temperature/K			Mass loss/%
	inflexion point	start	end	
1	443.0	417.8	472.4	0.2
2	580.4	514.9	607.2	12.4
3	624.1	607.2	635.4	4.9
4	684.1	635.4	745.3	22.0
5	924.7	871.1	982.3	5.1
6	1055.3	982.3	1085.7	2.7
7	1131.8	1085.7	1175.0	2.9
			total	56.6

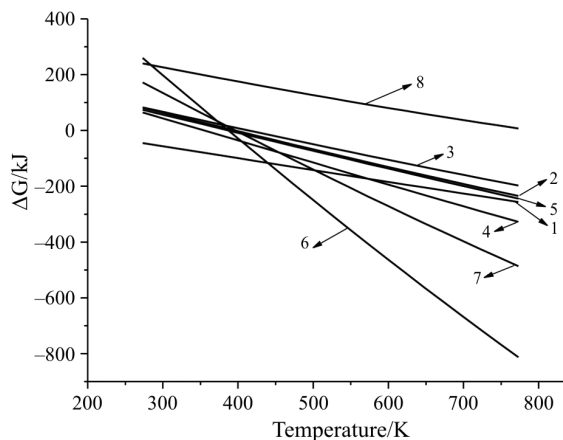


Fig. 1 Thermodynamical data for reactions (1)–(8) between ammonium sulphate and phosphate

Table 2 Mass loss during thermal decomposition up to 773 K ('Setaram') of TF+AS (mass ratio 1:1)

No.	Temperature/K			Mass loss/%
	inflexion point	start	end	
1	591.4	523.0	616.2	10.6
2	635.2	616.2	652.5	5.4
3	670.1	652.5	683.5	8.0
4	699.3	683.5	734.1	13.8
5	754.6	734.1	765.1	1.4
			total	38.7

The analysis of TG-DTG-DTA-dependencies related to the decomposition of TF and AS mixture (Fig. 2, Table 2) shows that the reactions are based on the behaviour of $(\text{NH}_4)_2\text{SO}_4$ [1]. A total of 56.6% mass losses were registered in the temperature range of 293–1273 K. The reactions occurring at temperatures up to 1273 K are determined by the registered mass losses and endo-effects at 580, 624, 684, 924, 1055, 1131 K that have formed three main transformation temperature ranges 500–700, 900–1000 and 1000–1150 K. The mass losses (39.3%) in the first temperature range (up to 700 K) show that the most intensive interactions occur at temperatures up to 700 K. The gas components emitted during decomposition of $(\text{NH}_4)_2\text{SO}_4$, such as NH_3 , SO_3 , H_2O form a suitable gas media for formation of ammonia-calcium ortho-, poly-, meta- and/or pyrophosphates, which is mentioned by other researchers as well [6–14]. The endo-effect occurring at 624 K and the stepwise character of the TG curves is an indication for reactions rate, resulting ammonia-calcium phosphates and follow up dehydration [14]. Our initial assumptions are confirmed by the results of the studies, using a Setaram thermal analyzer, coupled with a simultaneous evolved gas analyzer. The results are presented in Fig. 3 and Table 2.

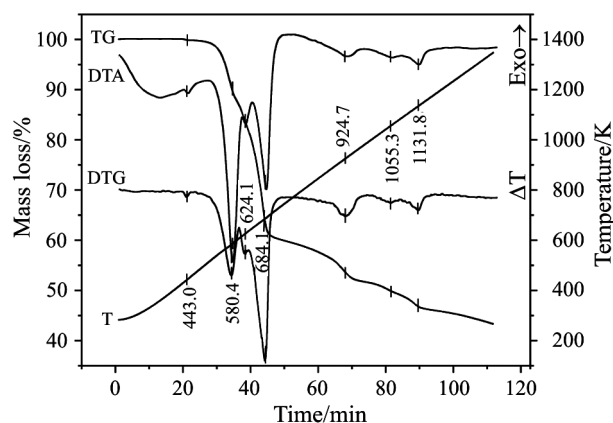


Fig. 2 TG, DTG, DTA curves of TF+AS mixture, 1:1, heated up to 1273 in air-medium

A data comparison from the two thermal analysers (Figs 2, 3 and Tables 1, 2) show a good coincidence concerning of registered mass losses and transformation temperature ranges. Differences in the data from the two apparatuses occur in the separation of the endothermal effects in the 620–750 K temperature range, and in the occurrence of small endothermic effects in the 730–770 K temperature range (Table 2), registered only with the Setaram analyser, where the sample mass is a little bit bigger. The gas analysis data provide additional evidences about reactions occurring between the components of the mixture in the 273–773 K temperature range. The concentrations of released gases coincide with the thermal effects registered on DTG-DTA curves in Figs 2, 3. Nitrogen from the system is emitted as am-

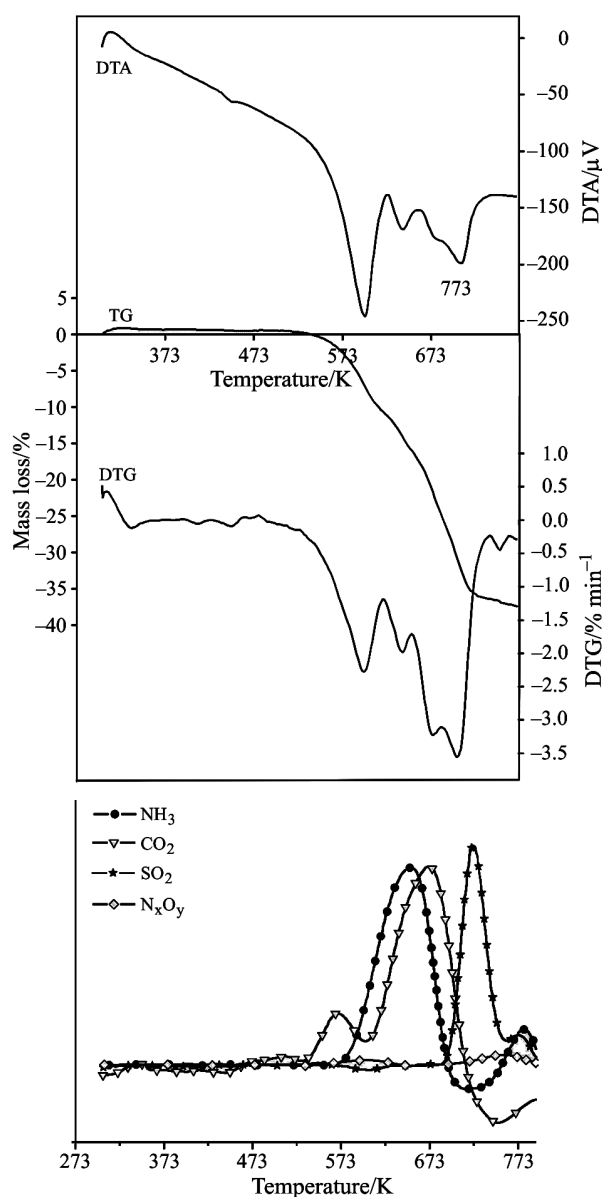


Fig. 3 Simultaneous TG-DTG-DTA curves with evolved gas analysis for TF+AS mixture, 1:1

monia at 648 and 780 K and as nitrous oxides at 603 and 755 K. Sulphuric oxides (such as SO_x) in waste gases are registered at 722 K (Fig. 3). These results confirm previous results of ours [1, 12, 13] and of other authors [6, 8, 9, 15] showing that during low-temperature range (500–650 K) AS starts to decompose and as a result mainly NH₄HSO₄ and ammonia are generated.

The emissions of sulphur oxides registered at 722 K prove that the NH₄HSO₄ is thermally unstable and starts to decompose, releasing ammonia and sulphur oxides. It is interesting to note that CO₂ emissions were registered at 570 K, a small peak, and at 670 K, a more intensive peak and it indicates decomposition of the carbonates (impurities in phosphorite). It can be noted that the peaks registering the presence of CO₂ in the off gases are almost identical with the ammonia peak. This proves that ammonia and carbon dioxide are probably products of the same reaction or of reactions occurring simultaneously. The registered amount of emitted ammonia and sulphur, carbon and nitrogen ox-

ides is only a part (Tables 2, 3) in comparison with the decomposition of chemically pure ammonium sulphate – 17.8% [1, 14]. Obviously, some of these gas components participate in secondary reactions.

X-ray powder diffraction analysis of initial, intermediates and final products from decomposition of a TF and AS mixture (1:1)

The results (Fig. 4) show that at temperatures up to 723 K calcium hydrogen-orthophosphates and hydrogen-pyrophosphates, as well as NH₄CaP₃O₉ are presented in the solid phase. The X-ray shows weak low-intensity diffraction lines of polyphosphate. When the treatment temperature is raised up to 973 K, α-Ca₂P₂O₇, Ca₃(PO₄)₂ and CaSO₄ are registered. The main phases in the end products at temperatures as high as 1273 K are Ca₅F(PO₄)₃, Ca₃(PO₄)₂, α-Ca₂P₂O₇ and CaSO₄.

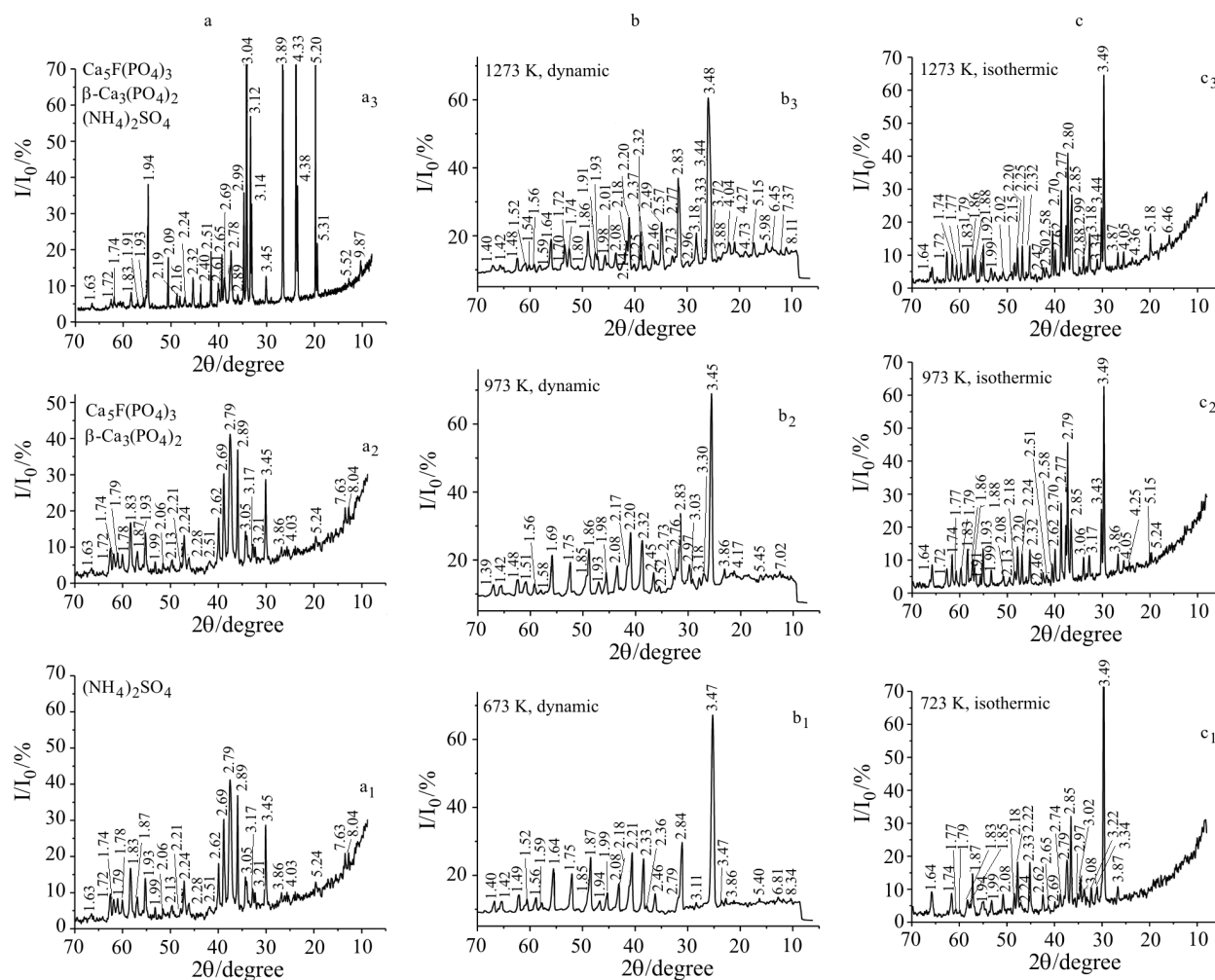


Fig. 4 X-ray diffraction intensities of a – raw materials, b – products after dynamic and c – isothermal heating

Electron microscope study of initial, intermediate and final products from decomposition of TF and AS mixture (1:1)

The results from the electron microscope analysis are presented in Figs 5a, b and c according to the heating rates and end temperatures. The presented electron mi-

croscope photographs (Fig. 5) indicate the change of habitues of particulates at various temperatures. The input component type features well expressed crystallites. When heated to 723 K, new phases start forming, and they are presented on the photographs by needle shaped and rounded crystalline forms (Figs 5b, c). Melting and agglomeration occur at temperature 1273 K.

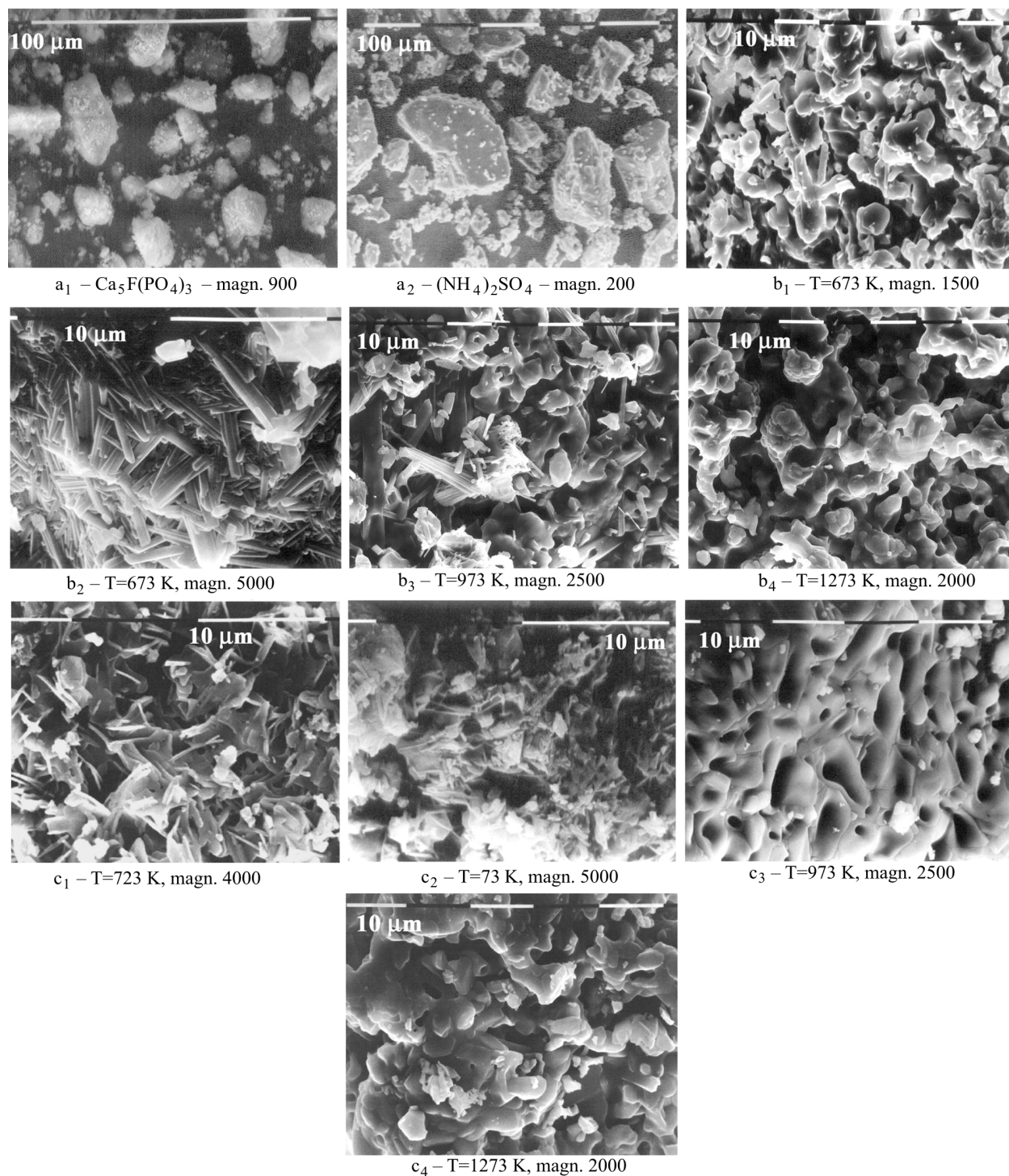


Fig. 5 Electron microscope photos of the a – raw materials, products after b – dynamic and c – isothermal heating

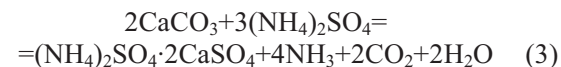
Infrared spectra of initial mixture, intermediates and final products from decomposition of TF and AS mixture (1:1)

The compounds formed during the thermal treatment were identified on the basis of identified functional groups. They are presented in Table 3.

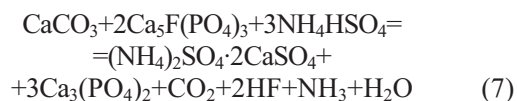
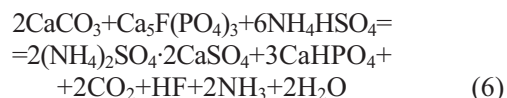
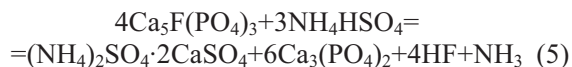
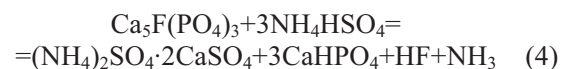
The infrared spectroscopy results are consistent with the X-ray powder diffraction analysis data. Unlike the X-ray powder diffraction analysis, the infrared spectroscopy data confirm deformation and stretching vibrations of CO_3^{2-} and it proves the presence of free CaCO_3 in the treated samples at temperatures up to 973 K – δCO_3 (865 cm^{-1}), $\nu_{\text{as}}\text{CO}_3$ ($1435, 1460$) (it is as an impurity in a phosphorite). The occurrence of the $\nu_{\text{as}}\text{CO}_3$ line at $1540\text{--}1560\text{ cm}^{-1}$ could be explained with the introduction of a carbonate ion in the structure of apatite and production of carbonate apatite. The line of asymmetric stretching vibration present in $\nu_{\text{as}}\text{SO}_4$ ($670\text{--}680, 1100\text{--}1120\text{ cm}^{-1}$) is evidence of sulphate in the samples, most likely NH_4HSO_4 and CaSO_4 , and only CaSO_4 at temperatures 973 K. When temperatures are higher than 673 K NH_4HSO_4 becomes thermally unstable. At 723 K in isothermal regime and 973 K in dynamic regime, pyrophosphates prevail in the solid phase products. At temperatures higher than 973 K (isothermal conditions) IR spectrums intensities are lower. The infrared spectroscopy data confirm the generation of $\text{CaH}_2\text{P}_2\text{O}_7$ by the presence of asymmetric stretching vibration lines – $\nu_{\text{as}}\text{OH}$ ($2420, 2780, 2800\text{ cm}^{-1}$) and deformation fluctuation – δOH ($1220, 1635, 1660$ and 1670 cm^{-1}) of OH groups where hydrogen participates in POH type acid ions with strong hydrogen links [1–7]. The lines $\nu_{\text{as}}\text{OH}$ ($1200\text{--}1220, 2300\text{--}2370\text{ cm}^{-1}$) prove the structurally bonded water in the phosphate ion presented as CaHPO_4 . The main phases in the final products of treatment at highest temperatures are $\beta\text{-Ca}_3(\text{PO}_4)_2$ and CaSO_4 .

Discussion

The results from the thermal analyses under various heating regimes and the X-ray powder diffraction and spectroscopic analyses, aimed to identify the intermediates and final products from thermal treatment of the phosphorite and ammonium sulphate mixture, prove formation of the following compounds: at temperature 653 K – $\text{NH}_4\text{HSO}_4, (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{CaSO}_4, \text{CaHPO}_4$; at 683 K – $\text{NH}_4\text{CaP}_3\text{O}_9$; at 733 K – $\text{Ca}_2\text{P}_2\text{O}_7$ and $\text{Ca}(\text{PO}_3)_2$; at 1273 K – the final phosphorous containing solid phase products are $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}_2\text{P}_2\text{O}_7$. The interactions occurring in the gaseous phase generate $\text{NH}_3, \text{CO}_2, \text{SO}_x$ and N_xO_y . The studies carried out using a set of physical methods suggest the following chemical mechanism of the thermal decomposition process:



607–653 K



653–683 K

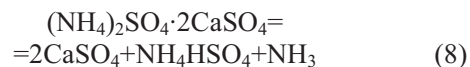
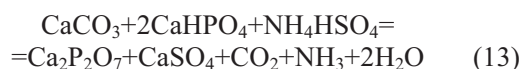
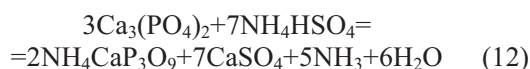
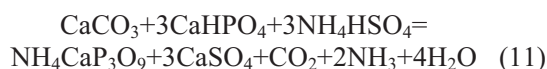
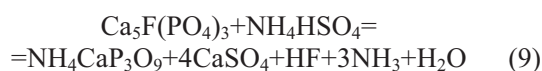
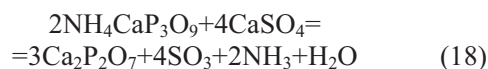
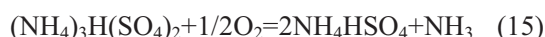
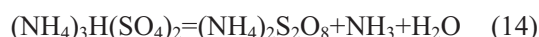


Table 3 Infrared spectroscopy data about intermediates and final products from thermal treatment of a TF and AS mixture (1:1) at different temperatures

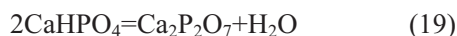
Temperature/K	Identified phases
	Dynamic heating regime
673	$\text{Ca}_5\text{F}(\text{PO}_4)_3, \text{CaCO}_3, \text{CaHPO}_4, \text{CaH}_2\text{P}_2\text{O}_7, \text{NH}_4\text{CaP}_3\text{O}_9, \text{CaSO}_4$
973	$\text{Ca}_5\text{F}(\text{PO}_4)_3, \text{CaCO}_3, \text{CaH}_2\text{P}_2\text{O}_7, \beta\text{-Ca}_2\text{P}_2\text{O}_7, \beta\text{-Ca}_3(\text{PO}_4)_2, \text{CaSO}_4$
1273	$\text{Ca}_5\text{F}(\text{PO}_4)_3, \text{CaCO}_3, \beta\text{-Ca}_3(\text{PO}_4)_2, \beta\text{-Ca}_2\text{P}_2\text{O}_7, \text{CaSO}_4$
	Isothermal treatment
723	$\text{Ca}_5\text{F}(\text{PO}_4)_3, \text{CaCO}_3, \text{CaHPO}_4, \text{CaH}_2\text{P}_2\text{O}_7, \beta\text{-Ca}_2\text{P}_2\text{O}_7, \beta\text{-Ca}_3(\text{PO}_4)_2, \text{NH}_4\text{CaP}_3\text{O}_9, \text{CaSO}_4$
973	$\text{Ca}_5\text{F}(\text{PO}_4)_3, \beta\text{-Ca}_3(\text{PO}_4)_2, \beta\text{-Ca}_2\text{P}_2\text{O}_7, \text{CaSO}_4$
1273	$\text{Ca}_5\text{F}(\text{PO}_4)_3, \beta\text{-Ca}_3(\text{PO}_4)_2, \beta\text{-Ca}_2\text{P}_2\text{O}_7, \text{CaSO}_4$



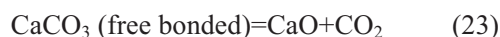
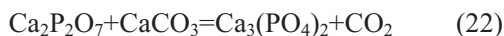
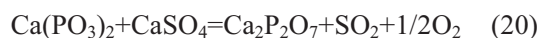
683–733 K



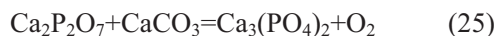
733–770 K



883–1033 K



1033–1273 K



The reactions that produce the highest mass losses in individual temperature ranges are 1, 8, 9, 13, 16, 20 and 26. The process of thermal decomposition of the mixture starts at 520 K (Figs 2, 3) with the breaking of one covalent bonds in the AS molecule and with reactions (1) and (2) occurring with an accompanying endo-effect at 580 K and mass loss of 12.4%. The registered mass losses are lower than the 17.8% registered for thermal decomposition of chemically pure AS in the same temperature range [1, 13]. This indicates that reactions (1) and (2) are not completed or that partly AS is involved in reaction (3). Endo effect at 624 K is and evidence about. Formation of $(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{CaSO}_4$ (reactions (3)–(5)) comes at temperatures close to 573 K. The results obtained are in a good agreement with from some other studies

[5, 8, 10–13]. Since the analysis of released gases prove that they contain CO_2 , it is obvious that reactions (4) and (5) occur simultaneously with reactions (6) and (7). The presence of CaHPO_4 in the products at 723 K and $\text{Ca}_2\text{P}_2\text{O}_7$ in the solid phase at temperatures at 973 K confirms the formation of pyrophosphates during an intermediate formation of hydrogen-orthophosphates (reactions (13) and (19)). Endo-effect registered in Fig. 3 755 K (1.4% mass loss) is also evidence about. Perhaps this is the decomposition temperature of the remaining CaHPO_4 that is accumulated in the system. Generation of $\text{NH}_4\text{CaP}_3\text{O}_9$ in the solid-phase products is possible under the interaction of $\text{Ca}_5\text{F}(\text{PO}_4)_3$, CaHPO_4 or $\text{Ca}_3(\text{PO}_4)_2$ with NH_4HSO_4 – reactions (9), (10), (12). The occurrence of CO_2 alongside NH_3 in the waste gases is a proof for reaction (11). The results from the analyses prove that the decomposition of $\text{NH}_4\text{CaP}_3\text{O}_9$ can produce $\text{Ca}(\text{PO}_3)_2$ and/or $\text{Ca}_2\text{P}_2\text{O}_7$ (reactions (17), (18)). This conclusion has been given also by Welch [10]. At temperature 1050 K transformation of $\text{Ca}(\text{PO}_3)_2$ to $\text{Ca}_3(\text{PO}_4)_2$ occurs (reaction (20)), and at temperature 1273 K – transformation of $\text{Ca}_2\text{P}_2\text{O}_7$ to $\text{Ca}_3(\text{PO}_4)_2$ via reactions (24) and (25) takes place. The high-temperature transformations of $\text{Ca}_2\text{P}_2\text{O}_7$ and $\text{Ca}(\text{PO}_3)_2$ to $\text{Ca}_3(\text{PO}_4)_2$ from these studies coincide with the results of Marraha [7, 8]. The process ends with the decomposition of structurally bonded carbonate in reaction (26).

The proposed chemical mechanism (reactions (1)–(26)) is not confronted with the conclusions of some other researchers [6–11], but the picture here is more detailed. The new elements are the reactions causing formation and thermal decomposition of intermediates from treatment of $(\text{NH}_4)_2\text{SO}_4$ (reactions (2), (14), (15) and (21)), proposed in our previous studies [1, 13, 14]. The phases identified in the low-temperature range (up to 723 K) by Pacak [10] and Welch [9] support the formation of $\text{NH}_4\text{CaP}_3\text{O}_9$ and CaHPO_4 . While Marraha [6, 7], Welch [10], Tonsuaadu [4, 5] believe that $\beta\text{-Ca}_3(\text{PO}_4)_2$ is the product only of high-temperature transformation of pyrophosphates, but the present data proves that $\beta\text{-Ca}_3(\text{PO}_4)_2$ is produced also in the low-temperature area alongside CaHPO_4 and CaSO_4 (reactions (5), (7)). These differences could be the result of some experimental parameters such as the partial pressure of gas components – NH_3 , SO_x and H_2O – which have not been the subject of the previous studies so far. From the results obtained it is obvious that the temperature heating rate and partial pressure of the generated gas components control the reaction rate. Formation of $\text{Ca}_3(\text{PO}_4)_2$ at lower temperatures may depend also on particle size, on sample quality, sample layer, crucible type, etc. Any way the phase studies of the solid and gas products and inter-

mediates prove that reactions generating major part of soluble phosphorous compounds occur in a temperature range 500–700 K. The phase composition of solid products and, respectively, the content of soluble phosphates could be controlled by the temperature and partial pressure of the main gas components. By selection of treatment conditions the mineral fertilizer characteristics could be controlled on the way to achieve the best agrochemical efficiency.

Conclusions

New data about thermal decomposition of phosphorite and $(\text{NH}_4)_2\text{SO}_4$ mixture in mass ratio 1:1 under dynamic and isothermal heating regime in air gas environment have been obtained. The intermediate and final solid-phase products have been characterized using X-ray powder diffraction and spectroscopic methods allowing identifying the main stages of structure changes in the system. The most intensive changes occur at temperatures up to 730 K. The formation of CaHPO_4 and $\text{NH}_4\text{CaP}_3\text{O}_9$ and their transformation to $\text{Ca}_2\text{P}_2\text{O}_7$, $\text{Ca}(\text{PO}_3)_2$ and $\text{Ca}_3(\text{PO}_4)_2$ has been proven. These data and the simultaneous analysis of the evolved gases show that the most suitable temperature treatment range is 500–700 K.

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