

Studies on the thermal behavior of a complex mineral fertilizer of nitrophosphate type

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Received 29 June 2005; received in revised form 5 September 2005; accepted 8 September 2005

Available online 7 October 2005

Abstract

This paper presents some studies on the thermal behavior of a complex mineral fertilizer of nitrophosphate type. The crystalline phases present in the initial fertilizer have been identified by means of X-ray diffractometry: NH_4NO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$. The processes occurring in the fertilizer when heated, have been elucidated comparing the TG and DTG curves of the fertilizer, with those of the present components and using the X-ray diffraction patterns of the products resulting after the thermal treatment of the fertilizer at various temperatures. © 2005 Elsevier B.V. All rights reserved.

Keywords: Complex mineral fertilizer; Nitrophosphate; Thermal behavior; X-ray diffractometry

1. Introduction

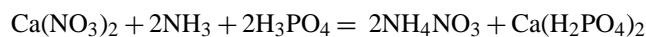
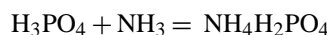
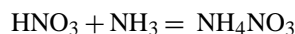
Complex mineral fertilizers of NP type (nitrophosphates) give the soil and therefore to plants too, two important primary macronutrients: nitrogen and phosphorus. This explains their wide use in agriculture. They are mainly composed of substances such as NH_4NO_3 (major component, 60–70%), $\text{NH}_4\text{H}_2\text{PO}_4$ and CaHPO_4 [1,2].

The obtaining process of nitrophosphates by decomposing phosphatic rocks with nitric acid consists in the following steps:

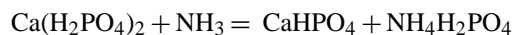
- decomposition of the phosphatic rocks with nitric acid; the solution obtained contains phosphoric acid, nitric acid, calcium nitrate, etc.;
- cooling of the solution, when the calcium nitrate partially crystallizes as $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$;
- separation of the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and obtaining of the NP solution containing phosphoric acid, nitric acid, the remaining calcium nitrate, etc.;
- neutralization of the NP solution with ammonia;
- concentration of the neutralized NP solution by evaporation and granulation of the melted reaction mass.

The most important step in the process of obtaining of the NP fertilizer is the neutralization of the NP solution with ammonia as it is crucial for the final composition of the fertilizer. The neutralization process of NP solution with ammonia is very complex. Its stoichiometry depends on the composition of NP solution, and on the pH of the reaction mass. The equations of the reactions in which the main components of the NP fertilizer result are as presented below:

Up to pH 2, the neutralization of nitric acid, the partial neutralization of phosphoric acid and the formation of calcium bis(dihydrogenphosphate) take place:



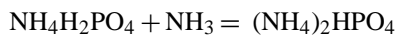
In the pH range 2–4, the complete neutralization of the phosphoric acid to the ammonium dihydrogenphosphate and the complete transformation of calcium bis(dihydrogenphosphate) in calcium hydrogen phosphate take place:



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In the pH range 4–6.5 the ammonium hydrogenphosphate is formed:



The studies on the thermal behavior and stability of the complex mineral fertilizers of NP type are significant for the steps of concentration of the NP solution and the granulation of the melted mixture. In industrial processes, evaporation takes place at temperatures up to 180 °C; at higher temperatures the decomposition processes of ammonium nitrate and ammonium phosphates accelerate, causing nitrogen loss [1].

2. Experimental

The complex fertilizer of NP type has been obtained from an industrial NP solution. The NP solution has been neutralized with 25% NH_3 solution, until the pH 6.5 was reached. For pH measurements a “Denver 250 pH-meter” has been used. The reaction mass was dried 24 h at 80 °C, grinded and sieved. We used the $-250 + 90 \mu\text{m}$ fraction.

The product was subjected to a complex study: determination of moisture content, chemical analysis, thermogravimetric analysis and X-ray diffractometry.

The moisture content has been determined by weighing the samples before and after drying; a “Denver analytical balance” has been used.

The phosphorus (total) content has been spectrophotometrically determined, using the molybdovanadophosphate method [3]. The absorbance of the solutions was gaged using a “Cary 50 spectrophotometer” at 400 nm.

The ammonia nitrogen content has been determined by titrimetric method [3].

The total nitrogen content has been determined by Devarda method [3].

The TG and DTG curves have been registered using a “Perkin-Elmer TGA7 thermobalance” controlled by a computer also used for the data acquisition. The non-isothermal experiments have been performed using linear heating rates, in controlled dynamic atmosphere (synthetic air, 10 mL min^{-1} flow rate), within the temperature range of 25–1000 °C, with samples of 60 mg.

The X-ray powder diffraction patterns have been registered with a “PHILIPS ‘XPRT PW 3020 diffractometer” (Cu $K\alpha$ radiation). We have registered the patterns of the initial complex mineral fertilizer of NP type and of the products resulting after its treatment at temperatures corresponding to the changes shown on TG and DTG curves (heating rate 1 K min^{-1}); the patterns have been recorded after cooling at room temperature.

3. Results and discussion

The chemical composition of the studied fertilizer was found: P_2O_5 —27.6%; $\text{N}_{\text{ammonium}}$ —19.2%; N_{total} —24.2%; humidity—5.7%; $\text{N}:\text{P}_2\text{O}_5$ (mass)—0.88.

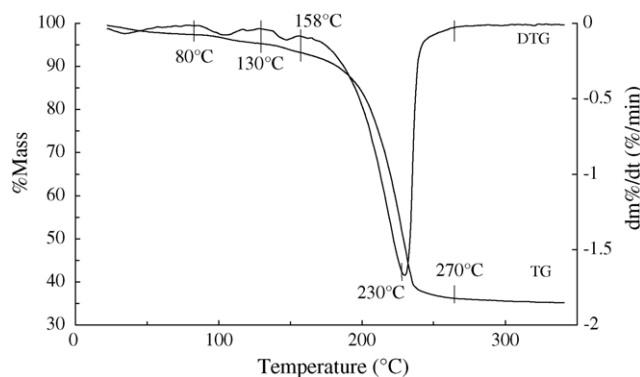


Fig. 1. TG and DTG curves of the complex mineral fertilizer of NP type.

The TG and DTG curves of the complex mineral fertilizer of NP type, registered with a heating rate of 1 K min^{-1} , are presented in Fig. 1.

During heating with a constant heating rate of 1 K min^{-1} up to 350 °C, four transformations accompanied by mass loss take place in the sample: (I) up to 80 °C, mass loss 2.7%; (II) between 80 and 130 °C, mass loss 1.9%; (III) between 130 and 158 °C, mass loss 2.0% and (IV) between 158 and 270 °C with maximum rate at 230 °C, mass loss 57.8%.

In order to identify the processes which cause each mass loss, the thermoanalytical curves of the sample have been compared with those of the compounds that could be present in the complex mineral fertilizer of NP type, according to the reactions mentioned in Section 1. In Fig. 2 are presented the TG and DTG curves of the NP sample and NH_4NO_3 (dried), and in Fig. 3 those of NP sample, $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ (registered with a constant heating rate of 10 K min^{-1}).

For the same purpose, there have been registered the X-ray diffraction patterns of the initial NP sample and after thermal treatment at various temperatures (Figs. 4–6). The initial sample contains some non-crystalline compounds and also three crystalline phases: NH_4NO_3 (crystalline form IV, stable at room temperature, orthorhombic) [4], $\text{NH}_4\text{H}_2\text{PO}_4$ (tetragonal) [5] and $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (orthorhombic) [6] (Fig. 4a). In the sample treated at 80 °C (a temperature that corresponds to the end of the first mass loss) the same crystalline phases as in the initial sample are present (Fig. 4b). In the pattern of the sample treated at 130 °C, the relative intensity of the

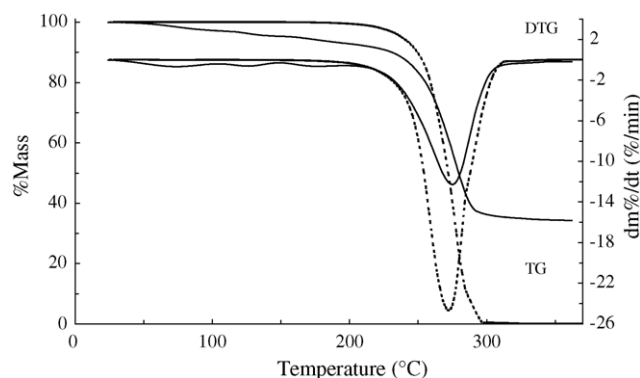


Fig. 2. TG and DTG curves of the NP fertilizer (—) and NH_4NO_3 (---).

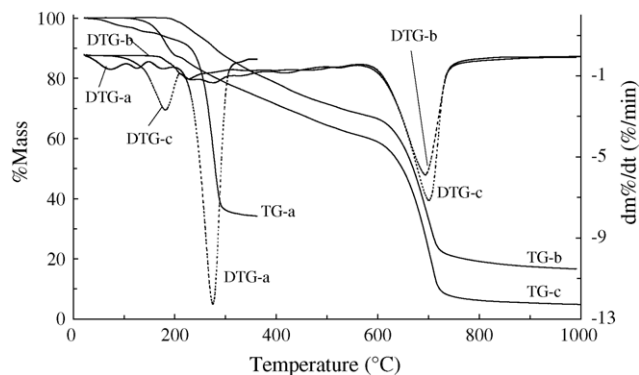


Fig. 3. TG (—) and DTG (---) curves of the NP fertilizer (a), $\text{NH}_4\text{H}_2\text{PO}_4$ (b) and $(\text{NH}_4)_2\text{HPO}_4$ (c).

lines of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ has decreased (the smallest disappeared, Fig. 5a). At 158°C , the temperature that corresponds to the end of the third process accompanied by mass loss (Fig. 1), only the lines of NH_4NO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ are still present (Fig. 5b). That proves the fact that up to this temperature, the substance $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ has suffered a transformation (dehydration or decomposition), the product being non-crystalline (there are no new lines in the patterns). The product of the thermal treatment of the sample at 350°C is non-crystalline (Fig. 5c).

In order to get more information on the processes that took place during heating, the sample was treated at higher temperatures, to study the crystallization of some amorphous compounds. At 600°C besides some non-crystalline compounds in

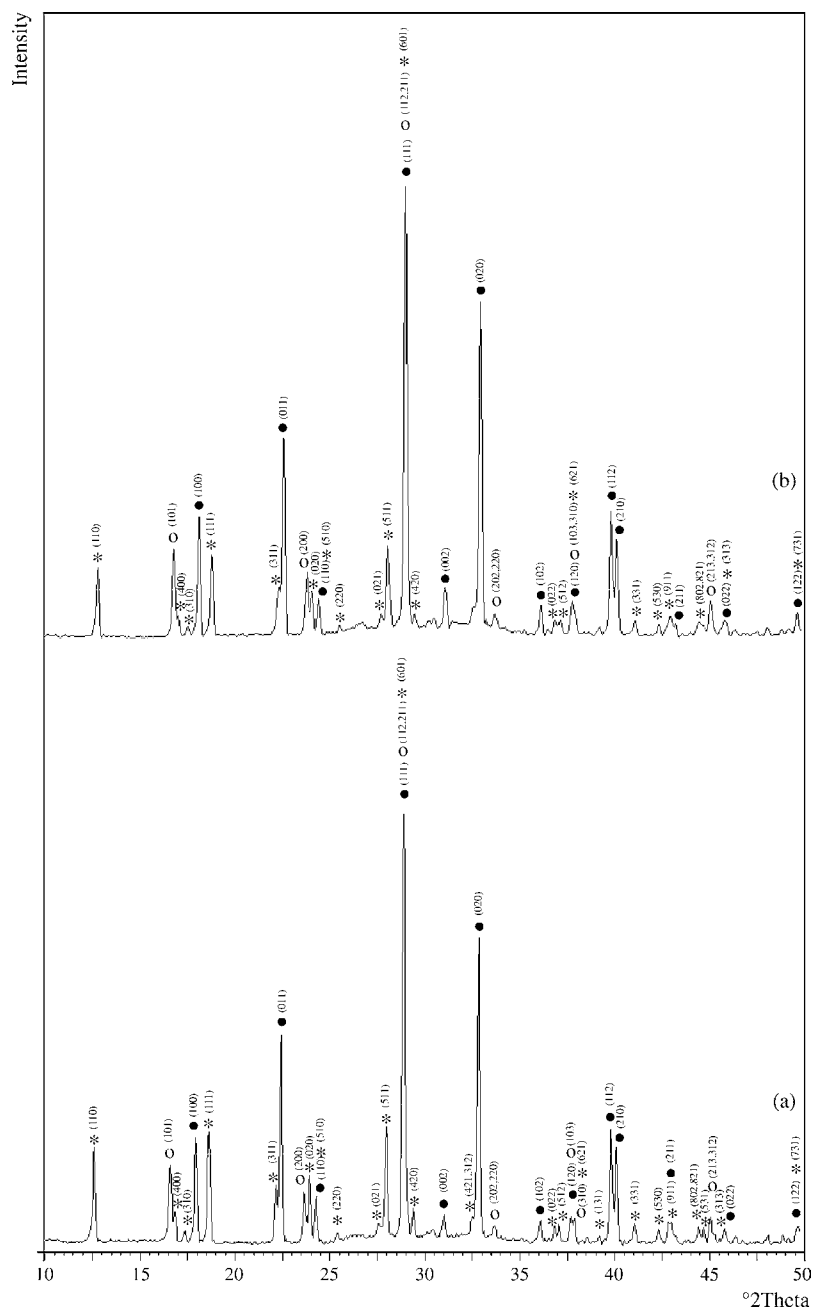


Fig. 4. X-ray diffraction patterns of the initial NP sample (a) and treated at 80°C (b) (●) NH_4NO_3 ; (○) $\text{NH}_4\text{H}_2\text{PO}_4$; (*) $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$.

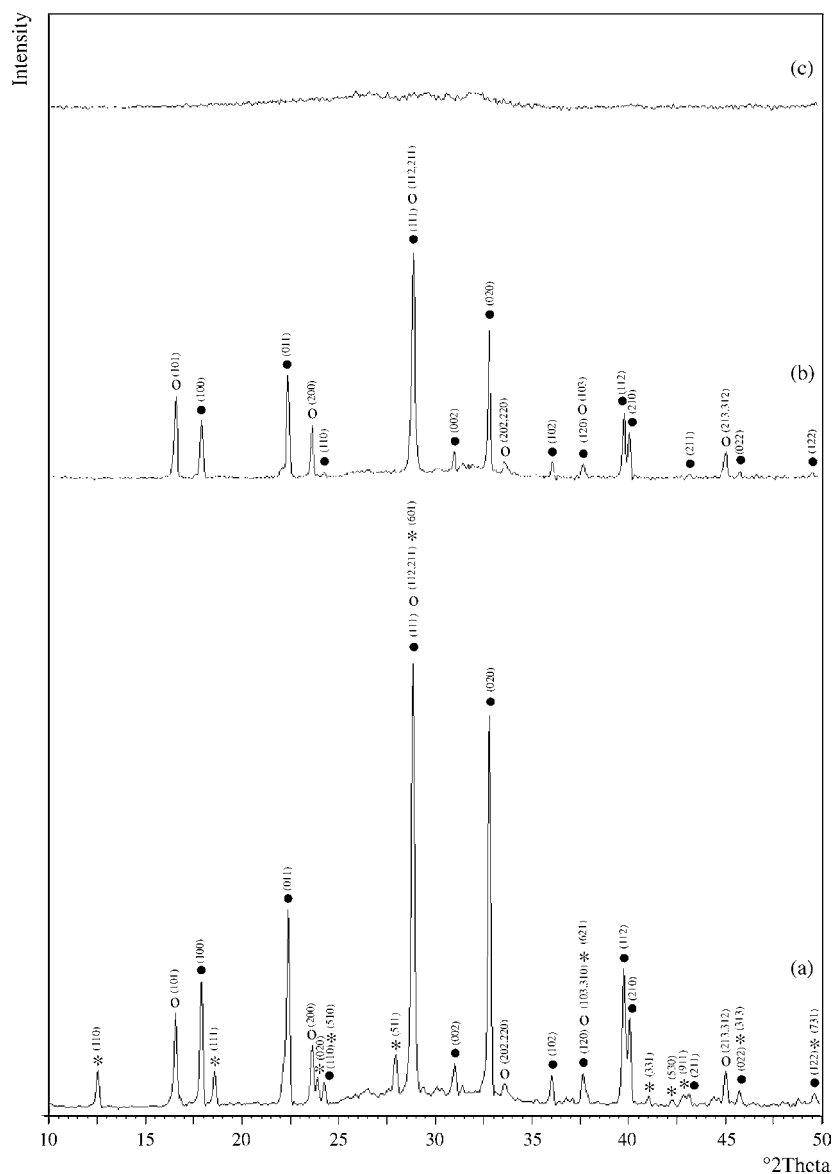


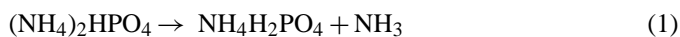
Fig. 5. X-ray diffraction patterns of the NP sample treated at 130 °C (a); 158 °C (b) and 350 °C (c) (●) NH_4NO_3 ; (○) $\text{NH}_4\text{H}_2\text{PO}_4$; (*) $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$.

the sample, two new crystalline phases are present: $\gamma\text{-Ca}_2\text{P}_2\text{O}_7$ [7] and $\text{Ca}(\text{PO}_3)_2$ [8] (Fig. 6a). At 800 °C, the sample contains the crystalline phases $\text{Ca}_4\text{P}_6\text{O}_{19}$ [9] and $\beta\text{-(CaP}_2\text{O}_6)$ [10] (Fig. 6b).

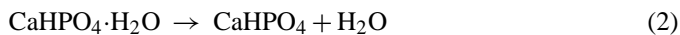
The mass loss I (up to 80 °C) is due to the loss of the adsorbed water.

The mass losses II and III (80–158 °C) are the results of the decomposition of some components present in small proportions in the sample, among them $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ identified by means of X-ray diffractometry. Its lines are not present anymore in the pattern, at the temperature corresponding to the end of the third mass loss (Fig. 5b). $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ may also be written as $(\text{NH}_4)_2\text{HPO}_4 \cdot \text{CaHPO}_4 \cdot \text{H}_2\text{O}$. In Fig. 3, one may notice that $(\text{NH}_4)_2\text{HPO}_4$ begins to decompose to $\text{NH}_4\text{H}_2\text{PO}_4$ by loss of ammonia at the temperature corresponding to the beginning of the second mass loss (80 °C); this decomposition ends at the temperature corresponding to the end of the

third mass loss (158 °C) [11]:



At 100 °C begins the dehydration of $\text{CaHPO}_4 \cdot \text{H}_2\text{O}$ [12]:



These transformations explain the decrease of the relative intensity of $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ lines at 130 °C and their complete disappearing at 158 °C.

Due to the fact that in the above patterns (Fig. 5a and b) there are no new lines, the resulting product CaHPO_4 is amorphous. The crystallinity of the $\text{NH}_4\text{H}_2\text{PO}_4$ formed during the decomposition of $(\text{NH}_4)_2\text{HPO}_4$ cannot be proved because it was already present in the initial sample.

Figs. 2 and 3 show that up to 158 °C NH_4NO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ are not decomposing, a fact also confirmed by the

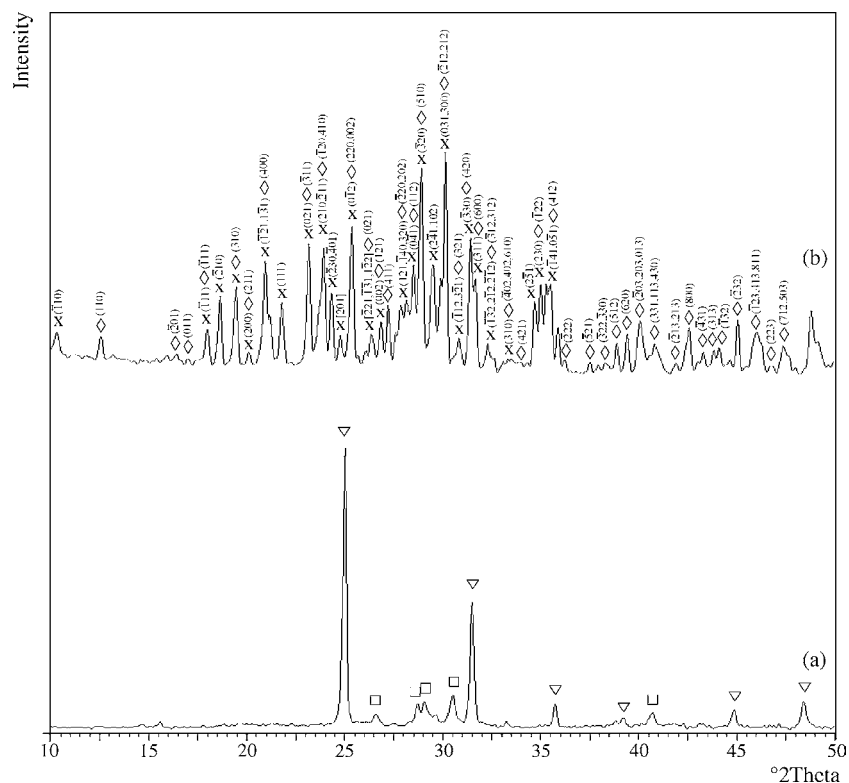


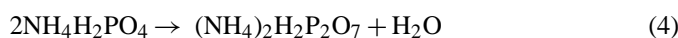
Fig. 6. X-ray diffraction patterns of the NP sample treated at 600 °C (a) and 800 °C (b) (□) γ - $\text{Ca}_2\text{P}_2\text{O}_7$; (▽) $\text{Ca}(\text{PO}_3)_2$; (×) $\text{Ca}_4\text{P}_6\text{O}_{19}$; (◇) β - (CaP_2O_6) .

presence of their diffraction lines in the pattern of the NP sample treated at this temperature (Fig. 5b).

The fourth mass loss is mainly due to the NH_4NO_3 that totally decomposes within this range of temperature [13] (Fig. 2):



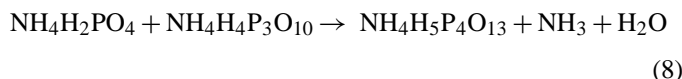
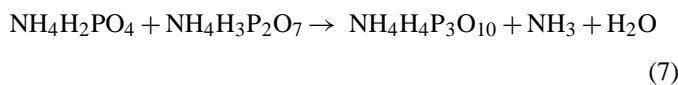
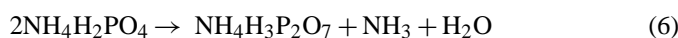
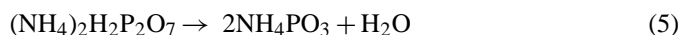
Within this range of temperature the decomposition of $\text{NH}_4\text{H}_2\text{PO}_4$ also begins [11] (Fig. 3). It was present in the initial sample and resulted at the decomposition of $(\text{NH}_4)_2\text{HPO}_4$ in a previous step:



and continues the dehydration of $\text{CaHPO}_4 \cdot \text{H}_2\text{O}$ according to reaction (2) [12].

The residue at 350 °C is of 35.5% and is non-crystalline (Fig. 5c). The IR spectrum of this residue confirms the decomposition of NH_4NO_3 (its characteristic frequencies disappeared); the intensity of NH_4^+ frequencies decreased and frequencies characteristic to the pyrophosphates appeared [14].

When the NP sample is heated at higher temperatures the decomposition of $\text{NH}_4\text{H}_2\text{PO}_4$ continues according to reactions (4)–(8) [15–17]:

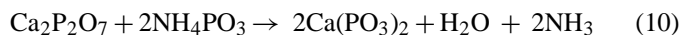


At temperatures higher as 400 °C the decomposition process slows down (Fig. 3) and the composition of the product goes to metaphosphate NH_4PO_3 [15–17].

Within this range of temperature the decomposition of CaHPO_4 begins [12]:

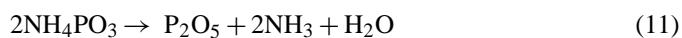


Reactions between the compounds formed up to this moment also take place:



Reactions (9) and (10) are confirmed by the fact that in the diffraction pattern of the NP sample treated at 600 °C the lines of the crystalline phases γ - $\text{Ca}_2\text{P}_2\text{O}_7$ and $\text{Ca}(\text{PO}_3)_2$ are to be found (Fig. 6a).

Analyzing the thermal behavior of $\text{NH}_4\text{H}_2\text{PO}_4$, one may notice that when heated at higher temperatures, the resulting NH_4PO_3 decomposes:



Once formed P_2O_5 , a sublimation process occurs within the range of temperature 570–840 °C (Fig. 3).

In the case of the NP fertilizer that we have studied, the mass of the sample remained practically the same, beginning with 550 °C. That leads to the conclusion that the reaction (11) did not take place, because NH_4PO_3 was consumed in reaction (10).

When the NP fertilizer is heated at higher temperatures, the condensation of the resulting phosphates occurs. At 800 °C in the sample the crystalline phases $\text{Ca}_4\text{P}_6\text{O}_9$ and $\beta\text{-(CaP}_2\text{O}_6)$ are present (Fig. 6b). The sample heated at 1000 °C is sintered and could not be taken from the crucible because a phosphatic glass was formed.

4. Conclusions

In our paper, the thermal behavior of a complex mineral fertilizer of nitrophosphate type was studied. When heated with a constant heating rate, up to 350 °C, the fertilizer submits four mass losses. The processes that cause the mass losses were elucidated by comparing the TG and DTG curves of the fertilizer, and those of the compounds that can be present in the sample (according to the stoichiometry of the obtaining process) and by means of X-ray diffraction patterns of the fertilizer, thermally treated at various temperatures.

By means of the X-ray diffractometry in the complex fertilizer of NP type three crystalline phases were identified: NH_4NO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$. Non-crystalline components are also present.

Up to 158 °C the fertilizer presents a relatively small mass loss, due to the loss of adsorbed water and to the decomposition of some components present in small proportions (loss of crystallization water and ammonia). Within the 158–270 °C range, considerable nitrogen loss takes place, due to the decomposition of the major component, the ammonium nitrate.

If the heating continues, the fertilizer losses slowly about 2% mass up to 550 °C as a result of the transformations of the other components. Condensations of the resulting products and reactions among them are taking place until at 1000 °C, a phosphatic glass is obtained.

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