Studies on Heat Treated Ammonium Phosphates with Boron

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A fertilizer based on ammonium phosphate with 5% (w/w) boron was obtained by neutralization of phosphoric acid with ammonia solution. Boric acid was added into the reaction mass at a 1.5 NH_3:H_3PO_4 molar ratio. The thermal analysis of the fertilizer obtained indicated an increase of thermal stability at temperatures above 475°C with increase of boron content. The X-ray diffraction of a heat treated sample indicated the appearence above 500°C of a single crystalline phase, boron orthophosphate, BPO_4. Further investigations of the sample by infrared analysis, scanning electron microscopy (SEM) and energy-dispersive X-ray microanalysis (EDAX) confirmed the results of X-ray diffraction. The formation of BPO_4 explains the increase of thermal stability at temperatures above 475°C. A new method of obtaining boron orthophosphate, by calcination of the fertilizer based on ammonium phosphate and boron added as boric acid was suggested.

Keywords: boron, boron orthophoshate, fertilizer, amonium phospshate, micronutrient

Boron is an essential micronutrient for plants. Plants respond only to boron activity in soil solution [1, 2]. Availability of boron to plants is influenced by soil factors as *p*H, texture, moisture, temperature, content and quality of organic matter and clay [3]. In arid and semiarid soils, to the high level of boron already present in the soil, supplemental quantities coming from the irrigation water are added. The toxic level of boron surpress plant growth. Boron deficiency is observed most likely in coarse textured soils, in regions with high humidity [4]. These soils have lower content of clay and organic matters, and present a low ability to adsorb boron and prevent leaching. Therefore, fertilizers with low solubility and slow release of boron into the soil, such as ulexite, are prefered. In this case, even the lowest fertilizator application rate, had a signifiant residual effect on soil available boron [5].

Boron is required in very small quantities, varying for different plant species, but the range between toxic and deficient level of its concentration in soil solution is narrower than for any other micronutrient [6, 7].

Boron compounds are usually mixed with a bazic fertilizer to maintain the recommanded application rate [8]. Some aspects have to be taken into consideration when preparing boron containing fertilizers. In order to establish the appropiate concentration of boron fertilizers applied, one has to considere the boron toxicity for plants with increasing boron application. The possibility of leaching boron from sandy soils is another problem associated with highly soluble boron compounds [9].

Boron orthophosphate BPO_4 is a very efficient boron containing fertilizer. It is not soluble in water, so boron orthophosphate is not washed from the soils by rainfalls. Although not soluble in water, when incorporated into soil, it slowly releases soluble boron. The release of boron from boron orthophosphate is believed to result from chemical reactions with substances present in soil [10].

In this paper a fertilizer based on ammonium phosphate with 5% boron added as boric acid was prepared. The thermal analysis of the product indicated an increase of its thermal stability at temperatures above 475°C, in comparaison with similar fertilizers with lower boron content [11, 12]. The objective of the studies was to investigate the possible formation of new chemical compounds of boron with the phosphates from the system and to explain the thermal behaviour of the fertilizer.

Experimental part

A fertilizer based on ammonium phosphate with boron as micronutient was obtained by neutralization of 50 mL phosphoric acid 43.5% P_2O_5, obtained from phosphoric acid 64.47% P_2O_5 (Merck, minimum 99%) with ammonia solution 25% (Reactivul Bucureşti), under continuos stirring at room temperature, up to *p*H 8.8. Crystalline boric acid (Merck, min.99.8%) was introduced into the neutralization mass at a 1.5 NH_3:H_3PO_4 molar ratio. All the reagents were of analytical grade. The fertilizer obtained was dried at 60°C.

The P_2O_5 content in dried products was determined by gravimetric analysis. The gravimetric determination of phosphorus was accomplished by its precipitation as magnezium ammonium phosphate hexahydrate $MgNH_4PO_4.6H_2O$ and conversion of the precipitate by calcination at 1000°C in magnezium pyrophosphate $Mg_2P_2O_7$ [13]. The nitrogen in ammonia was determined by spectrophotometric analysis in presence of Nessler reagent (λ = 425 nm) [14] and the boron content was determined by spectrophotometric analysis with carmine acid reagent (λ = 630 nm)[15, 16]. UV-VIS spectra were recorded using the Cary 50 spectrophotometer.

The thermal analytical curve TG and DTG have been obtained on a computer controlled NETZSCH TG 209 apparatus with K(NiCr-Ni) thermocouple, in an aluminium crucible, with a linear heating rate of 10°C min^{-1}, in the temperature range of 30 - 990°C, in dynamic atmosphere (nitrogen, 5 mL . min^{-1}), on a sample of about 10 mg.

The sample was further calcinated for 2 h at 500°C in a Nabertherm oven ignition with a heating rate of 10°C min^{-1}. The heat treated sample was subject to a complex study including X-ray diffraction, infrared analysis, scanning electron microscopy (SEM) and energy-dispersive X-ray microanalysis (EDAX) [17].

X-ray powder diffraction patterns were taken on a Bruker D8 Advance diffractometer, in Bragg-Brentano geometry, with graphite monochromatized CuK-α (λ=1.5418Å) radiation.

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Table 1
EXPERIMENTAL DATA CORRESPONDING TO THE CHEMICAL COMPOSITION OF SAMPLE E

Sample	P_2O_5/%	N-NH_4/ %	Massic ratio N:P_2O_5	Boron/ %
E	48.9	19.1	0,39	4.94

Table 2
MASS LOSSES AT HEATING OF SAMPLE E COMPARED WITH SAMPLES B-D [12]

Sample	Temp. range/ °C	Mass loss, %	Temp. range/ °C	Mass loss/ %	Temp range/ °C	Mass loss, %	Final residu e/ %
B	65-515	39.5	515-690	31	740-930	10.3	16.3
C	65-490	36.9	490-760	25.2	760-950	16	21
D	65-480	36.1	480-715	28.9	715-950	4	29.5
E	70-475	36	475-770	12.5	-	-	51.5

The infrared spectra in KBr matrix were run on a Jasko 410 spectrophotometer in the frequency range 4000-400 cm^{-1}. The microstructural investigation of the fertilizer obtained have been realized by scanning electron microscopy (SEM) and energy-dispersive X-ray microanalysis (EDAX) using an Inspect S microscope.

Results and discussion

The sample with 5% boron (named sample E) has been obtained through neutralization of phosphoric acid with ammonia and boric acid addition. Boron content was expressed as boron grams/100g diammonium hydrogen phosphate.

Chemical composition

The results of the chemical analysis are presented in table 1.

In accordance with the literature data [18-20] a mixture of ammonium dihydrogen phosphate (ADP) and diammonium hydrogen phosphate (DHP) was obtained.

Thermal studies

Thermal analytical curves (TG and DTG) obtained by heating sample E from 30 to 990°C with a rate of 10°C·min^{-1} are shown in figure 1.

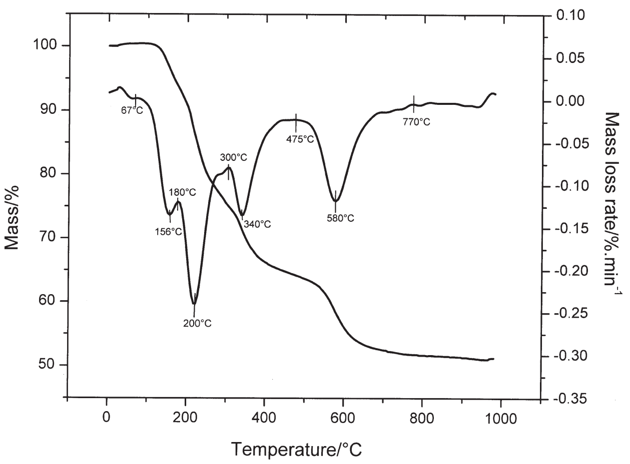

Fig.1. TG and DTG curves of sample E

The sample is stable up to 70°C. Between 70°C and 300°C the sample E undergoes a first process with mass loss, attributed to the DHP decomposition with ammonia release and ADP formation (equation 1). In the second stage, the mass loss was assigned to the decomposition of ADP to ammonium pyrophosphate and further to ammonium metaphosphate, according to the equations 2 and 3, and in agreement with literature data [21, 22] and to the liberation of water of constitution during polycondensation processes [23,24]. Ammonium metaphospate decomposes to P_2O_5 with ammonia and water evolution (equation 4).

$$(NH_4)_2HPO_4 \rightarrow NH_4H_2PO_4 + NH_3 \quad (1)$$

$$2NH_4H_2PO_4 \rightarrow (NH_4)_2H_2P_2O_7 + H_2O \quad (2)$$

$$(NH_4)_2H_2P_2O_7 \rightarrow 2NH_4PO_3 + H_2O \quad (3)$$

$$2NH_4PO_3 \rightarrow P_2O_5 + 2NH_3 + H_2O \quad (4)$$

The second process with mass loss takes place between 475 and 770°C and can be attributed to the sublimation of P_2O_5.

The complex process of thermal decomposition of the sample E represented by the equations 1-4 is overlapped with the thermal decomposition of boric acid, according to the equations 5 and 6 [12, 17].

$$H_3BO_3 \rightarrow HBO_2 + H_2O \quad (5)$$

$$2HBO_2 \rightarrow B_2O_3 + H_2O \quad (6)$$

The mass losses of the sample E and the corresponding temperature ranges are shown in table 2 in comparison with the similar data obtained by heating in the same temperature range of similar fertilizers with a lower content of boron according to table 2:

B, C and D (table 2) represent fertilizers based on ammonium phosphates with a content of 0.1, respective 0.5 and 1% boron [12].

From table 2 one can notice that up to about 475°C, the sample E undergoes similar mass losses with the samples with a lower boron content. Above 475°C and up to about 770°C, one can observe a decrease of mass loss with the increase of boron content, more evident at sample E, with a higher boron content (12.5% at sample E comparative to 28.9% at sample D). At temperatures above 770°C, the sample E is thermal stable. Consequently, the increase of boron (added as boric acid into the reaction mass) results in an increase of thermal stability of the fertilizer obtained at temperatures above 475-500°C.

A possible explanation of the thermal stability increase with increase of boron content above 475°C was the formation of a new chemical combination of boron with the phosphates present in the system. In order to investigate the new structure, the product E was calcinated at 500°C. The calcinated product, not soluble in water, was investigated by X-ray diffraction, infrared spectroscopy,

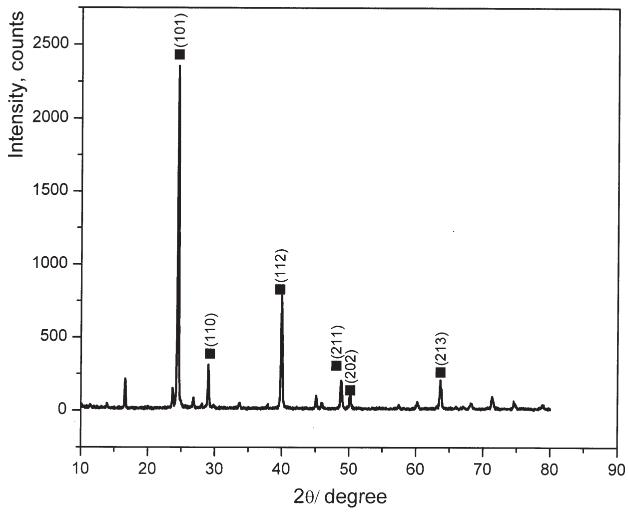

Fig. 2. X-ray diffraction pattern of the heat treated sample • BPO_4

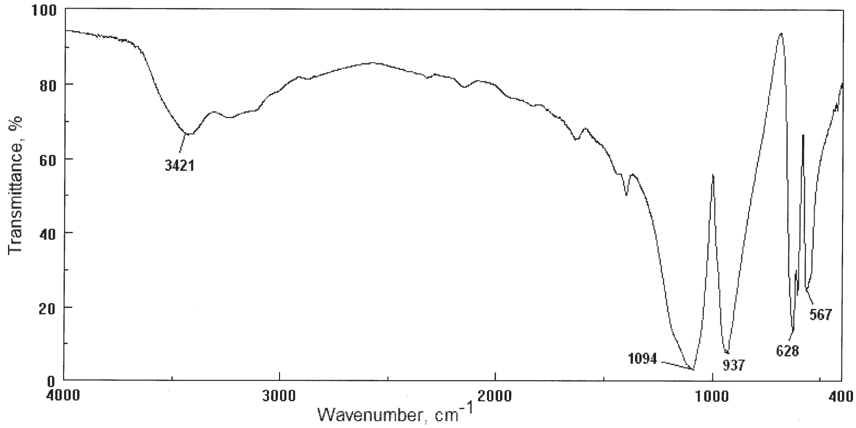

Fig. 3. Infrared spectrum of heat treated sample

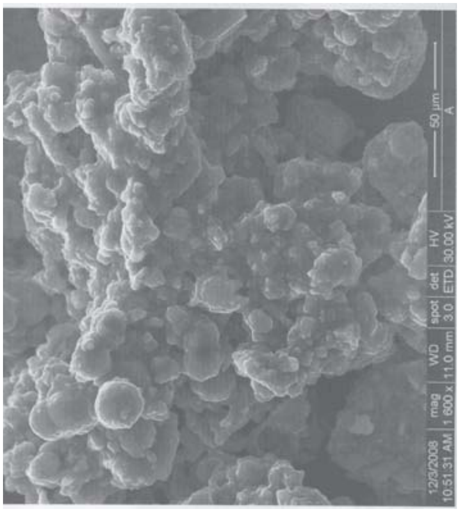

Fig. 4. SEM micrograph of the interface for sample E

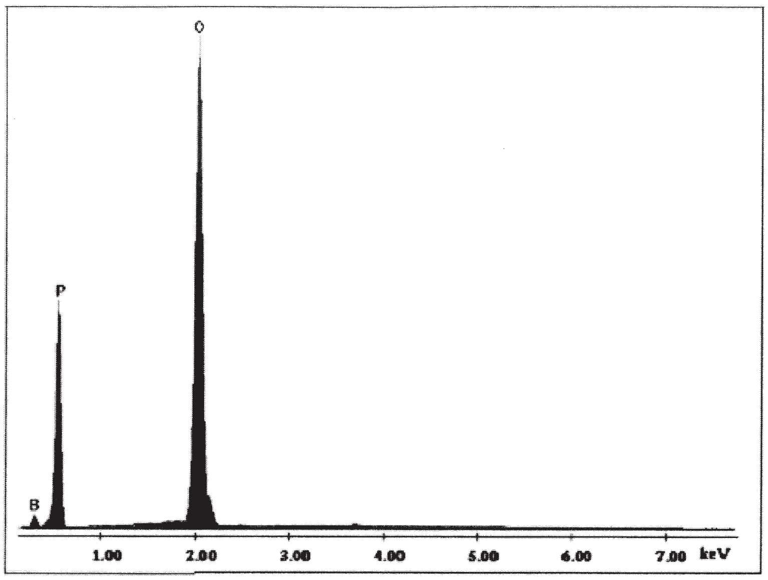

Fig. 5. EDAX spectrum of sample E

scanning electron microscopy (SEM) and energy-dispersive X-ray microanalysis (EDAX).

X-ray diffraction of heat treated fertilizer

X-ray patterns are shown in figure 2.

After calcination at 500°C, X-ray patterns indicated the presence of tetragonal boron orthophosphate, BPO_4 [25] as a single crystalline phase. The formation of BPO_4 can be explained by the reaction of B_2O_3, according to the equation 6 obtained by dehydration of boric acid and a part of P_2O_5 resulted during the process represented by the equation 4.

$$B_2O_3 + P_2O_5 \rightarrow 2BPO_4 \qquad (7)$$

FT-IR analysis

The IR spectrum of sample E (fig. 3) showed four characteristic intense bands at 1094, 936, 628 and 567 cm^{-1} assigned to boron orthophosphate (1085, 925, 615 and 550 cm^{-1}), slightly shifted towards higher frequences [26]. The bands at 3421-3423 cm^{-1} can be assigned to the water adsorbed in the time elapsed between thermal analysis and infrared spectrophotometry. Consequently, the data obtained by infrared spectroscopy confirmed the XRD data.

SEM/EDAX analysis

The SEM micrograph of the interface for sample E is presented in figure 4.

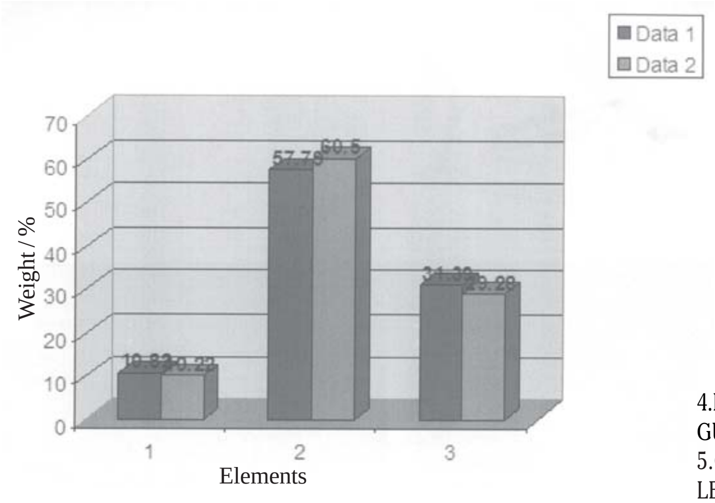

Fig. 6. Results of EDAX elemental analysis (data 1) in comparison with theoretic values (data 2)

The analized segment has the aspect of a conglomerate with dimensions up to 50μm.

The presence of P, B and O are showed in the EDAX spectrum.

One can observe that only P, B and O are present in the EDAX spectrum. The results of the elemental analysis showed that the concentration of the elements is in concordance with the concentration of the elements in the BPO_4 molecule. The results of the elemental analysis in comparison with the theoretic content of the elements in BPO_4 molecule are presented in figure 6.

The results of SEM/EDAX analysis were in concordance with X-ray diffraction and FT-IR analysis of the heat treated sample and confirmed the formation of boron orthophosphate BPO_4. The presence of thermal stable BPO_4 explains the increase of thermal stability above 475°C [27-29]. In addition, the BPO_4 formation induces an improvement of the fertilizer efficiency [10, 28].

Conclusions

The thermal analysis of a fertilizer based on ammonium phosphates with 5% boron, added as boric acid, showed an increase of thermal stability at temperatures above 475°C in comparison with fertilizers containing a lower boron content.

The XRD analysis of the fertilizer heated at 500°C showed the presence of boron orthophopshate BPO_4 as a single crystalline phase. The IR spectrum of the heat treated sample showed all the bands assigned to boron orthophosphate, which confirms the XRD data.

SEM/EDAX analysis emphasized the presence of a product with a chemical composition similar with the theoretic one corresponding to BPO_4. In conclusion, the formation of the thermal stable BPO_4 explains the increase of thermal stability of the boron containing fertilizer, with increase of boron content.

A new methode of obtaining boron orthophosphate has been proposed, by calcination of a fertilizer based on ammonium phosphates with boron added as boric acid at 500°C. The compound obtained is a high quality fertilizer, with slow boron release.

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