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PHASE CHANGES IN THE SYRIAN PHOSPHORITE–AMMONIUM SULPHATE SYSTEM
Mechanochemical activation

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With a complex of physico-chemical methods for analysis it is proved that in the course of mechanochemical treatment of a Syrian phosphorite and ammonium sulphate mixture new phases have been formed. The thermal analysis proves an increase in the reaction properties of the ammonium sulphate and the Syrian phosphorite which is a prerequisite for the increase in the content of $P_2O_5^{\text{assimilated}}$, in the activated phosphorite mixtures and the possibility to use them in the production of NP complex fertilizers.

Keywords: *ammonium sulphate, mechanochemical activation, phase changes, phosphorite, thermal analysis*

Introduction

The differential thermal method in combination with the X-ray phase and infrared spectroscopic analyses find application for proving the phase changes which have occurred in the process of mechanochemical activation [1, 2].

The aim of the present work is to investigate the possibility for solid phase synthesis in the process of mechanochemical activation of the not well-studied Syrian phosphorite mixed with ammonium sulphate.

Research methods

For the investigation aim Syrian phosphorite with the following chemical composition has been used: 29.5% $P_2O_5^{\text{total}}$; 6.9% $P_2O_5^{\text{assimilated}}$ (in 2% citric acid); 3.2% F; 46.5% CaO; 0.55% R_2O_3; (R=Al, Fe); 1.1% SO_3; 7.3% SiO_2; 0.35% MgO; 0.05% CI; 6.2% CO_2; moisture content 3.14% and average granulometric particles' composition 0.08 mm. The ammonium sulphate used, M=132.14; is characterized with a basic substance content – min. 99.5%. The mechanochemical activation has been carried out in a planetary mill Pulverisette-5, the Fritsch company (Germany) at a rotating speed of 320 min^{-1}, activation time from 5 to 300 min; type of the grinding bodies – plain steel, mass of the grinding bodies 510 g; diameter of the grinding bodies –20 mm. The sample mass for mechanochemical activation is 20 g, the mass ratio between the components – 1:1. The X-ray phase analyses were carried out with a diffractometer DRON, radiation CuK_α. The interplate distances are expressed in nm. The infrared spectral analysis was made on Spekord M-30 of Carl Zeis Jena in the absorption frequencies interval 3800–650 cm^{-1}. The thermal analysis was carried out on a thermal complex 'Stanton Redcroft' (England), at samples' mass 15.20±0.4 mg, in the temperature interval 288–1373 K, with a heating speed 10 K min^{-1}.

Results and discussion

Results from the X-ray phase analysis

The diffractograms of the phosphate mixtures activated with different durability register the formation of the following new phases: $Ca_3(PO_4)_2\cdot xH_2O$; $\beta(NH_4)_2H_2P_2O_7$; $(NH_4)_2SO_4\cdot 2CaSO_4$; $Ca_2P_2O_7$; $CaSO_4\cdot 2H_2O$ (Fig. 1). The chemistry of the processes which probably are performed in the process of the mechanochemical activation could be presented with the following reactions [1, 3]:

$$(NH_4)_2SO_4=NH_4HSO_4+NH_3 \quad (1)$$

$$2Ca_5F(PO_4)_3+6NH_4HSO_4=2(NH_4)_2SO_4\cdot 2CaSO_4+(NH_4)_2H_2P_2O_7+2Ca_3(PO_4)_2+2HF+H_2O \quad (2)$$

$$2Ca_5F(PO_4)_3+NH_4HSO_4=(NH_4)_2SO_4\cdot 2CaSO_4+Ca_2P_2O_7+2Ca_3(PO_4)_2+2HF+NH_3+H_2O \quad (3)$$

$$(NH_4)_2SO_4\cdot 2CaSO_4=2CaSO_4+2NH_3+SO_3+H_2O \quad (4)$$

The new proved compounds testify for the great irreversible changes which have occurred in the process of mechanochemical treatment and which probably lead to an increase in the dissolution of the activated phosphorite mixtures.

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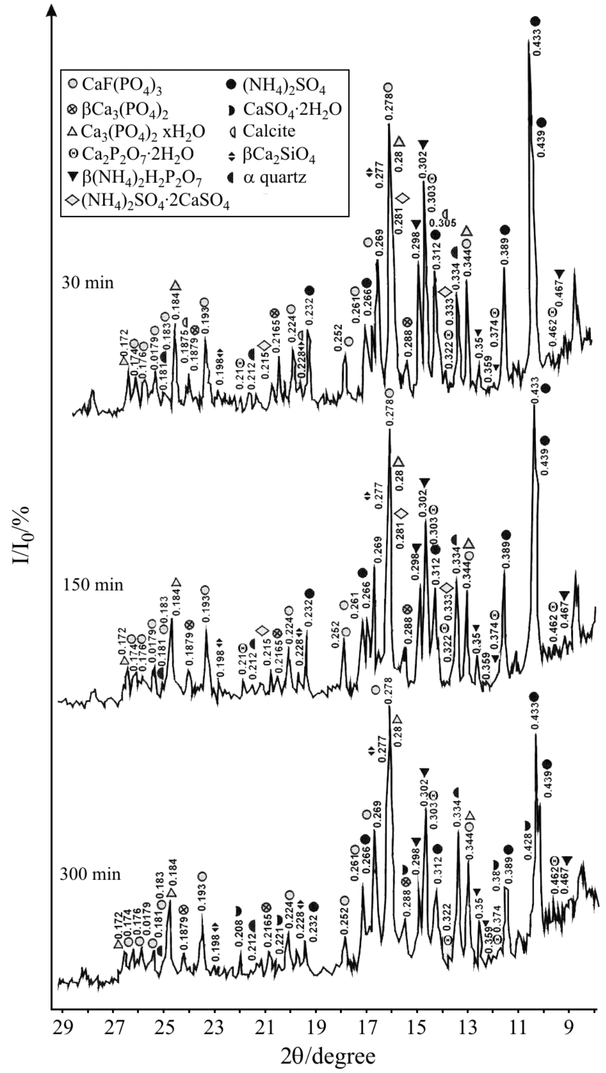

Fig. 1 Radiography of a phosphorite mixture activated 30, 150 and 300 min

In the activated phosphorite mixture which consists by Tunis phosphorite and ammonium sulphate [1] in contrast to the studied in the present paper phosphorite mixture which consists by Syrian phosphorite and ammonium sulphate a greater variety of ammonium–calcium polyphosphates are proved which probably can be explained with the different mineral origin of the natural phosphorites used. The Tunis phosphorite in contrast to the Syrian phosphorite is characterized by an increased content of SO_4^{2-}. According [4] the inclusion of SO_4^{2-} in the apatite structure leads to a decrease in the thermodynamic balance of its crystalline lattice and assists its more rapid destroying which can be explained by the higher chemical activation of the Tunis phosphorite in contrast to the Syrian phosphorite under mechanochemical activation.

Results from the infrared spectroscopy

With the increase of the duration of mechanochemical activation the infrared spectrum testifies for the increase of intensity of the absorption lines of the ammonium ion normal valency fluctuations: ν_1=3040 cm^{-1}; ν_2=1680 cm^{-1}; ν_3=3145 cm^{-1}; ν_4=1408 cm^{-1} [5] (Figs 2–3). This is clearly expressed with the samples activated for 150 min. Meanwhile the infrared spectra of the activated samples register the absorption lines of the normal fluctuations typical for $(NH_4)_2H_2P_2O_7$–$\nu_{s(P–O–P)}$=690 cm^{-1}; $\nu_{as(P–O–P)}$=865; $\nu_{s(PO_3)}$=985; $\nu_{as(PO_3)}$=1153; δ_{OH}=1170; δ_{OH}=1480; $\nu_{2(NH_4)}$=1650 and ν_4=1428 cm^{-1}) [6]. Since in the infrared spectrum of the ammonium ion active fluctuations are ν_3 and ν_4, the appearance of absorption lines in the valency no-degenerated fluctuations ν_1 and ν_2, testify for a symmetry violation of the ion. Probably in the process of mechanochemical treatment part of $(NH_4)_2SO_4$ is broken down and then forms $(NH_4)_2SO_4·2CaSO_4$ and $(NH_4)_2H_2P_2O_7$, which is in correlation with the results from the X-ray phase analysis. With an increase in the duration of the mechanochemical activation of the phosphorite mixtures to 150 min the normal valency fluctuation of SO_4^{2-} – ν_3 is split into two; and after 300 min into three: – ν_3=1108; ν_3=1120 and ν_3=1168 cm^{-1} [5]. This fact is due to the decrease in the ion symmetry which is typical for

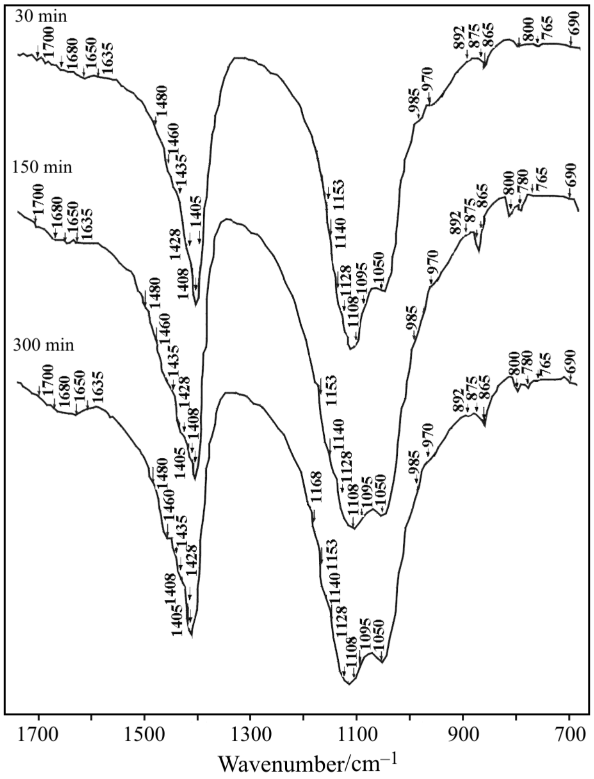

Fig. 2 Infrared spectra of phosphorite mixture activated: 30, 150 and 300 min

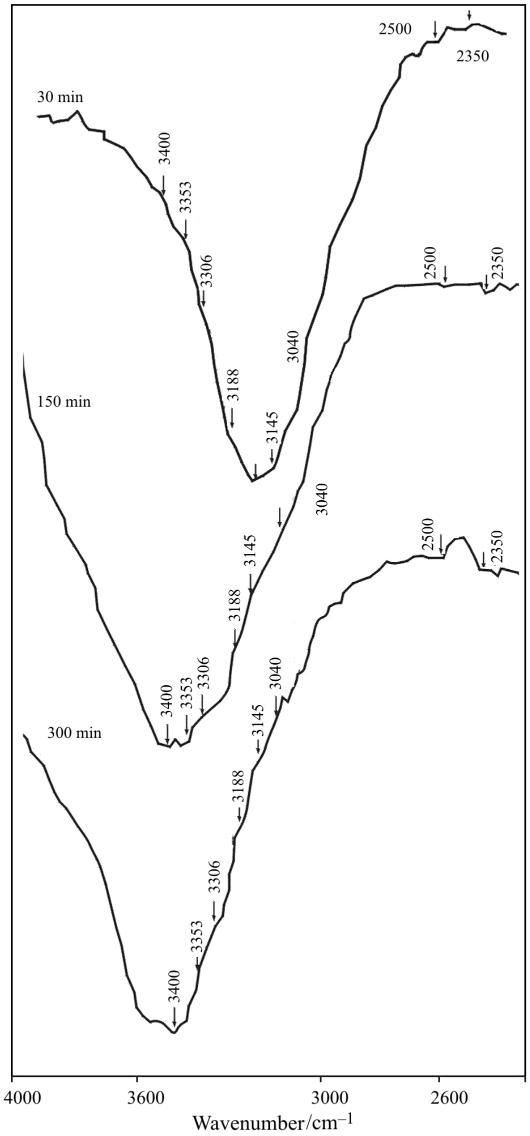

Fig. 3 Infrared spectra of phosphorite mixture activated: 30, 150 and 300 min

SO_4^2 in $CaSO_4$ towards SO_4^{2-} in $(NH_4)_2SO_4$ or in $(NH_4)_2SO_4{\cdot}2CaSO_4$. The registered changes are in correlation with the results from the X-ray phase analysis which prove the formation of $(NH_4)_2SO_4{\cdot}2CaSO_4$ and $CaSO_4$ in the process of mechanochemical activation. The quality changes in the symmetry phosphate group which is in the apatite structure composition are slightly expressed due to the strong influence of ν_3=1108 cm^{-1} in the SO_4^{2-} ion. A similar conclusion can be drawn concerning CO_3^{2-} because of the shield action of the intensive valency fluctuation of the NH_4^+ group – ν_3=1408 cm^{-1}. Meanwhile the infrared spectra of the activated samples prove the formation of $Ca_2P_2O_7{\cdot}2H_2O$–$\nu_{s(P–O–P)}$=765 cm^{-1}; $\nu_{as(P–O–P)}$=892 and $\nu_{as(PO_3)}$=1140 cm^{-1} [6], which confirms the results from the X-ray phase analysis.

Results from the thermal analysis

The analysis of TG-DTA dependencies from the decomposition of inactivated mixture Fig. 4 proves that the mechanism of the reactions which runs between the Syrian phosphorite and the ammonium sulphate is determined by the behaviour of the $(NH_4)_2SO_4$, as it is thermally more unstable composition. 43.0% mass loss were registered under the thermal treatment to 1316 K, and the intensive mixture break down is carried out in two temperature intervals 508-603 K; and 642–714 K. As a result of the chemical interactions between the reagents in the temperature interval 508–603 K, except for the basic reaction from the ammonium sulphate decomposition there are probably other interactions in which it is possible to get new compounds of the type $(NH_4)_2SO_4{\cdot}2CaSO_4$ and $CaHPO_4$. To prove the suggested assumption some endothermic effects are registered: 603–642 K, connected with the double salt's decomposition $(NH_4)_2SO_4{\cdot}2CaSO_4$ and 714–767 K, in which it is supposed that a dehydration of $CaHPO_4$ is made and $Ca_2P_2O_7$ is formed. In the high temperature interval up to 1346 K together with the thermal decomposition of the carbonate minerals it is probable to run a reaction between $Ca_2P_2O_7$ and the accumulated in the system $CaSO_4$ to the obtaining of $Ca_3(PO_4)_2$ (10).

The analysis of TG-DTA dependencies of the activated samples proves that there have occurred considerable changes in their course which are a result of the accumulation of the effects from the thermal interactions between the components of the mixture and the effects from the decomposition of the obtained under mechanochemical activation new phases (Figs 5–7). With an increase in the duration of the mechanochemical activation the thermal analysis registers appearance of new endothermic effects in the thermal curves of the activated samples. At the same time in the temperature interval 480–580 K it is registered a decrease in the temperatures of the thermal transformations with 40–50 K, compared to the inactivated mix-

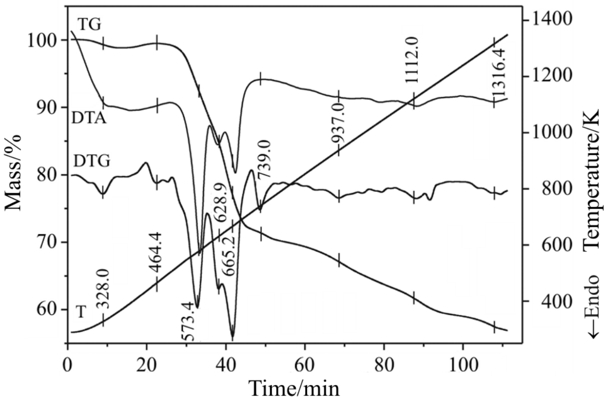

Fig. 4 TG-DTA analyses of the inactivated phosphorite mixture

ture. The registered changes are an indication for the increased reaction capability of the components of the activated phosphorite mixtures. The thermal analysis registers considerable difference in the dynamic of the mass loss. The thermal curve of the activated to 150 min sample registers an increase the total mass loss with about 3–4 points and a decrease with 3 points in the activated for 300 min sample compared to the inactivated sample. An interest represents the temperature interval 468–726 K, where intensive processes connected with the interaction of products obtained from mechanochemical synthesis under thermal treatment are carried out as well as their decomposition and the decomposition of the products obtained under thermal treatment. With an increase in the duration of mechanochemical activation the thermal analysis registers considerable decrease in the mass loss which is in correlation with the spectroscopic analyses. They prove the existence of considerable transformations in the phosphorite mixture in the course of the mechanochemical activation. In the temperature interval 418–479 K (Figs 5–7) connected with dehydration of the obtained in the process of mechanochemical activation $Ca_3(PO_4)_2{\cdot}xH_2O$ higher mass loss with the activated 150 and 300 min samples are registered compared to these registered with the activated for 30 min phosphorite mixture, which is an indication for an increase in its amount with an increased duration of mechanochemical treatment. The thermal curve of the activated for 30 min sample compared to the inactivated one and these of the activated for 150 and 300 min samples register endothermic effect (468–547 K), Which is probably due to decomposition of the obtained in the process of mechanochemical treatment double salt $(NH_4)_2SO_4{\cdot}2CaSO_4$ (4). Considerable changes occur in the temperature interval 468–548 K corresponding to the first stage in the decomposition of the ammonium sulphate (1) [3]. The thermal analysis registers an increase of two point's mass loss in the activated for 150 min sample compared to these registered in the activated for 30 min one and with one point compared to the activated for 300 min sample. Probably in the examined interval with the activated for 150 min, together with the decomposition of $(NH_4)_2SO_4$, runs a decomposition of the double salt obtained under mechanochemical activation. The registered changes are in correlation with the results from the spectroscopic analyses registering considerable transformations in the phosphorite mixtures when increasing the duration of the mechanochemical activation. It could be supposed that the lower mass loss in the activated for 300 min sample is due to the absence of the double salt in the activated sample. In the examined temperature interval it probably runs an interaction between the obtained under thermal treatment NH_4HSO_4 and the calcium fluorite apatite (2–3) [1]. To confirm the suggested assumption it is registered an endothermic effect (543–609 K) both with the inactivated samples and these ones activated for 150 and 300 min which effect is connected with the violating the structure of the double salt $(NH_4)_2SO_4{\cdot}2CaSO_4$ obtained in the process of thermal treatment. Probably similar processes but not so largely covered are carried out in the activated for 30 min sample. It could be supposed that in the ex-

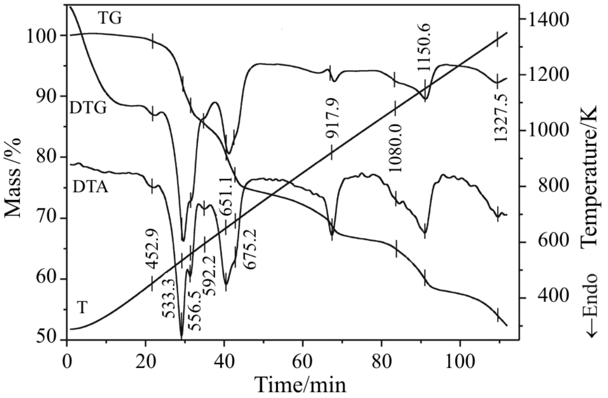

Fig. 6 TG-DTA dependencies of a phosphorite mixture, activated 150 min

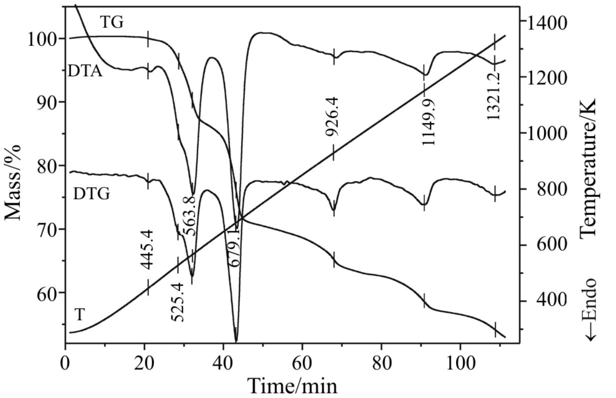

Fig. 5 TG-DTA dependencies of a phosphorite mixture, activated 30 min

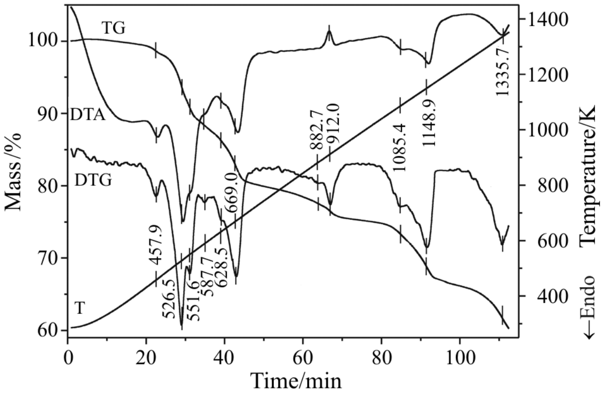

Fig. 7 TG-DTA dependencies of a phosphorite mixture, activated 300 min

amined interval in the activated for 300 min phosphorite mixture it runs an interaction between the obtained under the decomposition of the double salt $(NH_4)_2SO_4$ and the calcium fluorite apatite covering reaction (5) [7]. To confirm the suggested assumption it is registered in its thermal curve an endothermic effect (667–724 K), probably connected with transformation of the obtained in the process of thermal treatment $NH_4CaP_3O_9$ to $Ca(PO_3)_2$ (6) [7].

$$Ca_5F(PO_4)_3+4(NH_4)_2SO_4=NH_4CaP_3O_9+4CaSO_4+NH_4F+6NH_3+3H_2O \quad (5)$$

$$2NH_4CaP_3O_9+CaSO_4=3Ca(PO_3)_2+2NH_3+SO_3+H_2O \quad (6)$$

The registered changes in the dynamics of the mass loss in the activated for 150 min sample testify for the increased reaction capability of the phosphorite mixture components.

The thermal curves of the activated for 150 and 300 min samples in contrast to the activated for 30 min sample register in the temperature interval 580–618 K an endothermic effect in which it is probably completed a dehydration of the obtained in the process of mechanochemical activation and thermal treatment $(NH_4)_2H_2P_2O_7$, (this is proved by the spectroscopic analyses) forming $CaH_2P_2O_7$ or $Ca_2P_2O_7$. The changes which have occurred give us reason to suppose that with an increase in the duration of mechanochemical activation it is increased the reaction capability of the obtained new phases. It could be supposed that similar processes but not so largely covered are carried out in the activated for 30 min sample for which testify the higher mass loss in the temperature intervals: 875–975 K; 1282–1349 K.

The registered in the thermal curve of the activated for 300 min sample endothermic effect in the temperature interval 607–636 K, is probably due to the transformation of $Ca_2P_2O_7$ in $Ca(NH_4)_2P_2O_7$ covering reaction (7).

$$Ca_2P_2O_7+2NH_4HSO_4=Ca(NH_4)_2P_2O_7+CaSO_4+SO_3+H_2O \quad (7)$$

$$Ca(NH_4)_2P_2O_7=Ca(PO_3)_2+2NH_3+H_2O \quad (8)$$

Probably in the temperature interval 651–724 K, which is connected with the second stage of the decomposition of ammonium sulphate runs a decomposition of $Ca(NH_4)_2P_2O_7$ too (8). The registered changes in the mass loss dynamics in the activated for 300 min sample confirm the suggested assumption that in the process of mechanochemical treatment the reaction capability of the products from the mechanochemical synthesis is increased. This is a prerequisite for the increased content of $P_2O_5^{\text{assimilated}}$ in the activated samples. In the next temperature interval 875–975 K, it probably runs a dehydration of $CaH_2P_2O_7$ (9) [1].

$$CaH_2P_2O_7+Ca_3(PO_4)_2=2Ca_2P_2O_7+H_2O \quad (9)$$

The decarbonization of the phosphorite mixtures runs in the high temperature interval and in contrast to the inactivated mixture is performed in two stages. The first endothermic effect in the temperature interval 1040–1118 K is connected to the liberation of the introduced during the mechanochemical activation CO_3^{2-} ion. At the same time the thermal curves of the activated for 150 and 300 min samples register an exothermic effect which is not present during the thermal decomposition of the inactivated mixture and in the activated for 30 min sample. The appearance of exothermic effect is probably a result from the relaxation of the accumulated mechanical energy and testifies for an increased energy state of the components of the activated samples with an increase in the duration of the mechanochemical treatment – a prerequisite for their reaction capability. In the second temperature interval 1036–1195 K the registered endothermic effect is explained with the thermal decomposition of carbonate minerals accompanying the apatite. In the high temperature interval (1249–1351 K), in both the inactivated and the activated mixtures runs an interaction between the accumulated in the solid phase $CaSO_4$ and $Ca_2P_2O_7$ to obtain $Ca_3(PO_4)_2$ covering reaction (10).

$$Ca_2P_2O_7+CaSO_4=Ca_3(PO_4)_2+SO_3 \quad (10)$$

With an increase in the duration of the mechanochemical activation to 300 min some considerable enthalpy changes occur which find expression in considerable mass loss increase testifying for the transformation of the obtained in the process of mechanochemical activation and thermal treatment phosphorite mixtures $Ca_2P_2O_7$ in $Ca_3(PO_4)_2$ covering reaction (10). The registered change in the mass loss dynamics is in correlation with the results from the spectroscopic analyses.

Conclusions

The results from the spectroscopic and thermal research of a mixture of Syrian phosphorite and ammonium sulphate are subjected in advance to mechanochemical activation and give us reason to draw the following conclusions.

- The proved by the spectroscopic and thermal analyses new phases: $Ca_3(PO_4)_2{\cdot}xH_2O$; $\beta(NH_4)_2H_2P_2O_7$; $(NH_4)_2SO_4{\cdot}2CaSO_4$; $Ca_2P_2O_7{\cdot}2H_2O$; $CaSO_4{\cdot}2H_2O$, testify for the accomplishing of a mechanochemical synthesis in the process of mechanochemical activation.
- The results from the thermal analysis gives us reason to suppose that with an increase in the duration of mechanochemical activation the components of

the phosphorite mixtures and the obtained in the process of mechanochemical activation new phases increase their reaction capability which is a prerequisite for the increased content of $P_2O_5^{assimilated}$ in the activated samples and the possibility to use them in the production of NP complex fertilizer.

- The low content of some of the registered by spectroscopic analyses new phases makes their proof by thermal analyses difficult, which necessitates the continuation of studies in this branch.

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