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INFLUENCE OF TRIBOACTIVATION CONDITIONS ON THE SYNTHESIS IN NATURAL PHOSPHATE-AMMONIUM SULPHATE SYSTEM

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No data is available in the literature about the effects of mechano-chemical activation on the processes of chemical interaction in the Tunisia phosphorite-ammonium sulphate mixture. The purpose of this paper is to study the chemical and thermal reactions in mixtures of Tunisia phosphorite and ammonium sulphate in a mass ratio of 1:1, triboactivated in a planetary mill using different mill balls for a period of 10 h. Using chemical, thermal, X-ray powder diffraction and infrared spectroscopy to analyse the activation products, and analysing the changes occurring during the TG-DTA-DTG measurements, allowed to determine the chemical transformations in the system and to assess the degree of transformation of non-soluble forms of phosphorus from the natural phosphate into soluble. Data from the studies have registered the changes in the solids resulting from preliminary mechano-chemical activation of samples. The additional endo- and exothermic effects resulting from thermal decomposition in the temperature range of up to 1373 K are proof of the changes during the TG-DTA-DTG studies and of new interactions occurring in the system.

The results from the thermal and spectroscopic methods show that triboactivation using different mill balls and modes of operation produce new compounds in the form of ortho-, pyro- and tripolyphosphates, soluble in the soil solution. The data obtained are part of the complex studies on the way to optimize the composition and conditions of triboactivation and subsequent thermal treatment aimed to produce high-efficiency slow-acting fertilizer products.

Keywords: *ammonium sulphate, natural phosphate, polyphosphates, thermal decomposition, triboactivation*

Introduction

Low-temperature thermal tribochemical treatment of natural phosphates in a mixture with suitable reagents (polyproducts and industrial waste in some cases) is a perspective method for production of new types of balanced integrated NPS and NPKS fertilizers. Changes occurring in the natural phosphates-ammonium sulphate system during their treatment are subject of scientific interest [1–5]. The possibilities to produce new fertilizers through the introduction of sulphur as an additional nutritious element are the aim of the studies on the interactions in the system. The main objective is to obtain end products with higher content of plant-absorbable forms of P_2O_5 [6, 7]. No data is available in the literature about the effects of the experimental conditions of the mechano-chemical activation on the processes of chemical interaction in the Tunisia phosphorite-ammonium sulphate mixture.

The aim of the study is to investigate the chemical and thermal reactions in mixtures of Tunisia phosphorite (TF) and ammonium sulphate (AS) in mass ratio of 1:1, triboactivated in a planetary mill with chromium–nickel, zirconium and agate grinding balls for 10 h, by analysing the products of activation using chemical, thermal and spectroscopic methods and X-ray powder diffraction analysis.

Experimental

The investigation was based on the use of Tunisia phosphorite of the following composition (mass%): $29.58P_2O_5$, $48.40CaO$, $6.48CO_2$, $3.58SO_3$, $1.88SiO_2$, $2.74F$, $1.38Na_2O$, $0.07K_2O$, $0.056Cl$. The ammonium sulphate (AS) was pure, analysis grade /pa/ with catalogue No. 0140, ‘Alerus’, containing 99.5% AS. The mechanical and chemical activation of mixtures of Tunisia phosphorite and ammonium sulphate was carried out using a planetary mill Pulverisette-S, by Fritsch (Germany) at maximum speed and activation time of 10 h; type of the grinding balls – chromium–nickel, zirconium and agate, total – 140. The mass of the triboactivation samples was 20 g, with a mass ratio of the components of 1:1.

The degree of transformation of insoluble into soluble forms of P_2O_5 in non-activated and activated samples of TF and AS was assessed on the base of soluble P_2O_5 content in 2% of citric acid, consistent with the Bulgarian State Standard 13418-80. The

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thermal analysis was carried out using the thermal complex 'Stanton Redcroft' (England), with sample masses of 15.20±0.4 mg, in temperature range of 288–1373 K, and heating rate of 10 K min^{-1} in static air environment. X-ray powder diffraction analyses were conducted using a DRON diffraction metre, with CuK_α radiation. The X-ray powder diffraction 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 Zeis Jena in an interval of 650–4600 cm^{-1}.

Results and discussion

The results from the chemical, X-ray powder diffraction and thermal analyses of non-activated and triboactivated samples of Tunisia phosphorite and ammonium sulphate mixtures are presented in Figs 1–5 and Tables 1 and 2. The data about the degree of transformation of non-soluble P_2O_5 into soluble forms in a 2% citric acid for the non-activated mixture and for samples activated over 10 h in a planetary mill using different mill balls is as follows: 27.6% for the resulting untreated mixture, 55.2% for chromium–nickel, and 52.5% for the zirconium and agate mill balls. Chemical analysis data indicate an almost two-fold increase in the degree of transformation of non-soluble forms of P_2O_5 into soluble forms. A comparison of the results for different mill balls shows a higher degree of transformation using chromium-nickel mill balls and identical transformation using the other two types. The degree of transformation values prove the positive effect of preliminary mechanical and chemical activation of the mixtures and characterize the structural and chemical changes in the studied system. They can be related to changes in the structure of apatite and/or occurrence of irreversible chemical reactions and production of new phases with P_2O_5 present in soluble form.

X-ray powder diffraction analysis

The compounds identified in the solid products are presented in Table 1. The X-ray charts show significant reduction of the peak intensities in mechanically activated samples as compared to the peaks of non-activated mixtures, which is an indication of occurring amorphousness during treatment of samples in the planetary mill.

A comparison of the data from the X-ray powder diffraction analysis (Table 1) shows that when using agate and zirconium mill balls, the new phases that occur are $Ca_3(PO_4)_2 \cdot xH_2O$, $(NH_4)_2SO_4 \cdot 2CaSO_4$, $CaH_2P_2O_7$, α-$Ca_2P_2O_7$, $NH_4CaP_3O_9$. The use of chromium–nickel mill balls has not shown any $(NH_4)_2SO_4 \cdot 2CaSO_4$, but there was proven presence of $CaSO_4 \cdot 2H_2O$ as an independent phase. These data show that treatment has resulted in substantial changes in the phase composition of the studied mixtures. It is obvious that these changes are caused by energy from the friction and impact by the mill balls which create conditions for occurrence of structural defects in the output components. The resulting metastable conditions are a pre-requisite for the mixing of components at atomic and molecular levels [10–12]. Such a close contact favours chemical interactions in locally disturbed crystal structures resulting in the registered new solid phases $(NH_4)_2SO_4 \cdot 2CaSO_4$, $NH_4CaP_3O_9$, $Ca_3(PO_4)_2$, $CaH_2P_2O_7$, α-$Ca_2P_2O_7$ (Table 1) derived during the activation process. It is interesting to note that the no reflexes have been registered in the activated mixtures of other ammonia–calcium (calcium) hydrogenorthophosphates. This means that triboactivation violates the common rule about catenation of P–O–P chains of hydrogenorthophosphates [9] and perhaps they occur through direct synthesis consistent with following reactions:

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

$$NH_4HSO_4=NH_3+SO_3+H_2O \qquad (2)$$

$$\begin{aligned}&2Ca_5F(PO_4)_3+4NH_4HSO_4=\\&=(NH_4)_2SO_4 \cdot 2CaSO_4+CaH_2P_2O_7+\\&+2Ca_3(PO_4)_2+CaSO_4+2HF+2NH_3+H_2O\end{aligned} \qquad (3)$$

Table 1 Data from the X-ray powder diffraction analysis of non-activated mixtures and of samples activated using different mill balls

Sample	Identified phases
TF+AS, 1:1	$(NH_4)_2SO_4$, $Ca_5F(PO_4)_3$, β-$Ca_3(PO_4)_2$
Cr–Ni mill balls	$Ca_5F(PO_4)_3$, $(NH_4)_2SO_4$, β-$Ca_3(PO_4)_2$, $Ca_3(PO_4)_2 \cdot xH_2O$, $CaH_2P_2O_7$, α-$Ca_2P_2O_7$, $NH_4CaP_3O_9$, $CaSO_4 \cdot 2H_2O$
Zr mill balls	$Ca_5F(PO_4)_3$, $(NH_4)_2SO_4$, β-$Ca_3(PO_4)_2$, $Ca_3(PO_4)_2 \cdot xH_2O$, $(NH_4)_2SO_4 \cdot 2CaSO_4$, $CaH_2P_2O_7$, α-$Ca_2P_2O_7$, $NH_4CaP_3O_9$
Agate mill balls	$Ca_5F(PO_4)_3$, $(NH_4)_2SO_4$, β-$Ca_3(PO_4)_2$, $Ca_3(PO_4)_2 \cdot xH_2O$, $(NH_4)_2SO_4 \cdot 2CaSO_4$, $CaH_2P_2O_7$, α-$Ca_2P_2O_7$, $NH_4CaP_3O_9$

$$Ca_5F(PO_4)_3+6NH_4HSO_4= =2(NH_4)_2SO_4{\cdot}2CaSO_4+ +NH_4CaP_3O_9+HF+NH_3+3H_2O \qquad (4)$$

$$2Ca_5F(PO_4)_3+3NH_4HSO_4= =(NH_4)_2SO_4{\cdot}2CaSO_4+ +Ca_2P_2O_7+2Ca_3(PO_4)_2+2HF+NH_3+H_2O \qquad (5)$$

It can be assumed that the proceeding of reactions (1)–(5) is possible only through tribo-energy introduced into the system, since the mechanism of their generation is related to intermediary formation of $CaHPO_4$ [8, 9]. Despite the complexity and multi-variance of the chemical reactions, the formation of compounds containing the P_2O_7-group is energetically dominant. It is the calcium-ammonia meta- and hydrogen-pyrophosphates produced during the reactions (3)–(5) that increase the soluble forms of P_2O_5 in the products. It is obvious that the occurrence of $CaSO_4$ phase structures in the products of mechanical and chemical activation is linked to the preliminary disintegration of $(NH_4)_2SO_4$ to NH_4HSO_4, NH_3, H_2O and SO_3.

IR spectroscopy

The transformations to $(NH_4)_2SO_4{\cdot}2CaSO_4$, $Ca_3(PO_4)_2{\cdot}xH_2O$, $NH_4CaP_3O_9$, $CaH_2P_2O_7$, $Ca_2P_2O_7$ are confirmed also by the results from the infrared spectroscopy and thermal analysis. The results from the studies using infrared spectroscopy of non-activated mixture of TF and AS, 1:1 and mechanically and chemically activated samples in a planetary mill are presented in Fig. 1. The results from the infrared spectroscopy of the non-activated mixture of Tunisia phosphorite and ammonium sulphate prove the presence in its spectrum of the main functional groups of PO_4^{3-} ion based on all three stretching vibrations: $\upsilon_s=970\ cm^{-1}$ – fully symmetrical stretching vibration; δ – double degenerated stretching vibration; $\upsilon_{as}(F_2)=1050\ cm^{-1}$ ($P–O_I$); $\upsilon_{as}(F_2)=1110\ cm^{-1}$ ($P–O_{III}$); $\upsilon_{as}(F_2)=1140\ cm^{-1}$ ($P–O_{II}$); – asymmetrical triple degenerated stretching vibration. Apart from the main characteristic lines of phosphorite, the lines $\delta\ CO_3=865$, $\nu_{as}\ CO_3=1430$, $1465\ cm^{-1}$, that can be attributed to the free-bonded $CaCO_3$ in the phosphorite structure are also present. The $(NH_4)_2SO_4$ spectrum is characterized by stretching vibrations and deformation fluctuations of the NH_4^+ ion – $\upsilon_s\ NH_4=3000\ cm^{-1}$; $\delta\ NH_4=1570\ cm^{-1}$; $\upsilon_{as}\ NH_4=1400\ cm^{-1}$ and of SO_4 at $\nu_{as}\ SO_4=670–680\ cm^{-1}$, $1100–1120\ cm^{-1}$ and $\nu_s\ SO_4=970\ cm^{-1}$. The spectrums of activated mixtures reflect the structural changes resulting from the impact and presence of the intensities of functional groups that prove the formation of new phases. The presence of the line of asymmetrical stretching vibration of SO_4 at $\nu_{as}\ SO_4=650\ cm^{-1}$ alongside the three other lines at $\nu_{as}\ SO_4=1100\ cm^{-1}$, $\nu_s\ SO_4=3140\ cm^{-1}$, and those of the NH_4^+ ion – $\upsilon_s\ NH_4=3040–3080\ cm^{-1}$ in the spectrums indicates the presence of $(NH_4)_2SO_4{\cdot}2CaSO_4$ in the activated samples. The same absorption lines can be attributed to the NH_4HSO_4, but the shift of the line at $650\ cm^{-1}$ is an indication of $CaSO_4$, respectively, $(NH_4)_2SO_4{\cdot}2CaSO_4$ present in the samples. Another characteristic line in the infrared spectrums occurs at $725–730\ cm^{-1}$ and alongside the characteristic lines at $1100\ cm^{-1}$ are attributed to ν_s POP and $\nu_s\ PO_3$ of the $P_2O_7^{4-}$ ion, and the lines of asymmetrical stretching vibration – ν_{as} OH at $2600–2800\ cm^{-1}$ are attributed to hydrogen in acidic ions with strong hydrogen links [11]. This confirms the results from the X-ray powder diffraction analysis about presence of $CaH_2P_2O_7$ and $Ca_2P_2O_7$ in activated mixtures. The presence of metapolyphosphate is established by the lines of $\nu_{as}\ PO_2$ of $P_3O_9^{3-}$ at $1260–1310\ cm^{-1}$ and particularly those of $\nu_s\ NH_4$ at $3040\ cm^{-1}$ and $\nu_{as}\ NH_4$ at $1400\ cm^{-1}$. The occurrence of new lines at $1520–1540\ cm^{-1}$, attributed to CO_3 groups introduced into the structure of fluorapatite is particularly interesting. This phenomenon was registered also by Chaikina [10]. According to Chaikina, activation of CO_2 from air produces two forms of carbonate fluorapatite, B and AB. The lines present in the area $1520–1540\ cm^{-1}$ prove that our samples are more likely to form AB type of carbonate fluorapatite where the carbonate group is localised in the OH group along the axis 6_3 and in the Ca^{2+} vacancies, with partial replacement of the phosphate group [10]. These results are directly dependent on the mechanical and chemical activation of samples using different mill balls. The free-bonded water in the studied samples is proven by the presence of stretching vibration and deformation fluctuation lines for the OH ion in the areas 1650–1670 and $3300–3600\ cm^{-1}$. The multitude of absorption lines of free-bonded moisture determines the presence of most of the identified phases in the form of crystal-hydrates – $Ca_2P_2O_7{\cdot}xH_2O$, $Ca_3(PO_4)_2{\cdot}xH_2O$. The infrared spectrum data for the activated samples confirm the structural changes of phosphorite and are similar to the results from the X-ray powder diffraction analysis.

Thermal analysis of a non-activated mixture of TF and AS, 1:1

The analysis of the TG-DTA-dependencies of disintegration of a non-activated mixture (Fig. 3) proves that the reactions occurring between the Tunisia phosphorite and ammonium sulphate are determined by the behaviour of $(NH_4)_2SO_4$ as a compound of lower thermal stability. The mass losses registered at 49.2% when a temperature 1373 K was reached. The interaction of

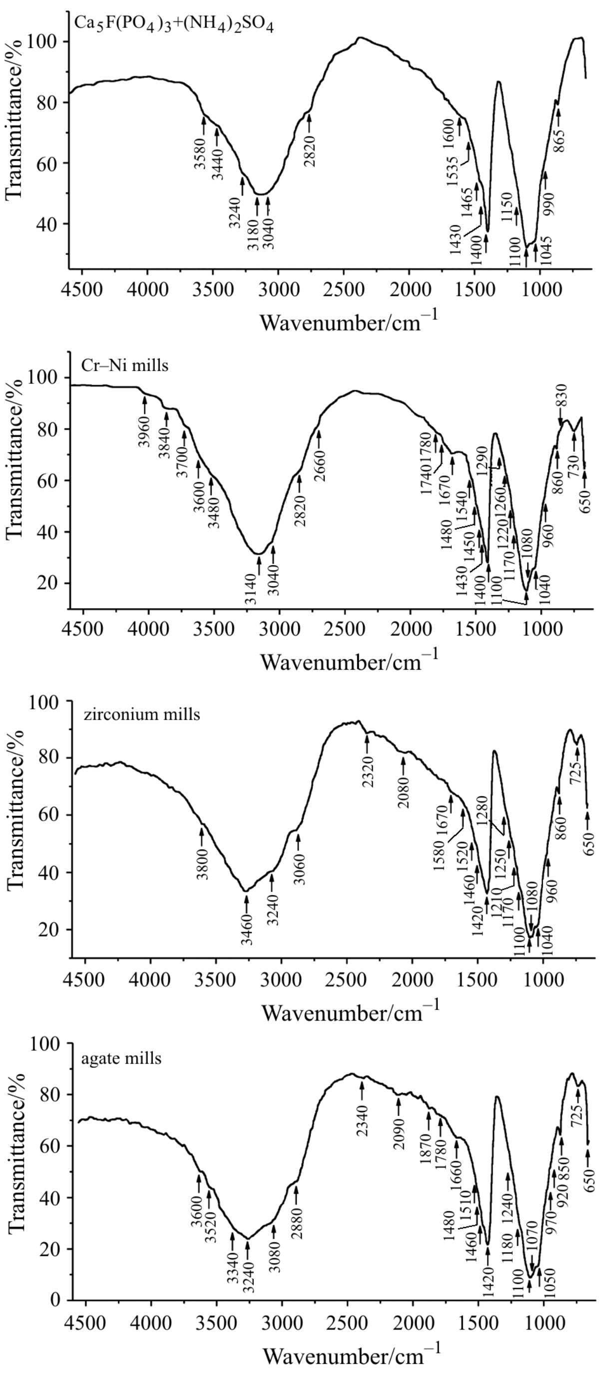

Fig. 1 Infrared spectrum intensities for TF+AS samples with mass ratio 1:1 – initial mixture and activated mixtures (10 h in a planetary mill with different grinding balls)

components in the temperature range of 523–643 K results not only in the main reactions from disintegration of ammonium sulphate, but also interactions producing the registered new compounds $(NH_4)_2SO_4{\cdot}2CaSO_4$, $CaHPO_4$ and $Ca_3(PO_4)_2$. Except for $CaHPO_4$, the phases are the same as those identified in the activated mixtures. Obviously, the intermediary products from NH_4HSO_4 and $CaHPO_4$ interact in the temperature range 633–673 K, resulting in generation of $NH_4CaP_3O_9$, $CaSO_4$ and α-$Ca_2P_2O_7$ in the system. The temperature range of 683–733 K allows for transformation of $NH_4CaP_3O_9$, to $Ca(PO_3)_2$ and $Ca_2P_2O_7$, which leads to the formation of new quantities of α-$Ca_2P_2O_7$. The next temperature range (1033–1173 K) allows for interaction between α-$Ca_2P_2O_7$ and the $CaSO_4$ accumulated in the system to produce $Ca_3(PO_4)_2$ [4, 9].

Thermal analysis of Tunisia phosphorite and ammonium sulphate mixtures activated in a planetary mill

The TG-DTA-dependencies derived at during the thermal analysis of activated mixtures are presented in Figs 2–5 and Table 2. The analysis of TG-DTA-dependencies shows that they are similar to the mixtures activated with chromium–nickel, zirconium and agate mill balls. Endothermic effects are registered in close temperature ranges: 313–333; 543–563; 662–693, 843–943 and 1113–1233 K. A drop in the total mass losses of approximately 7–12% was registered as compared to the non-activated mixture. Also, new endoeffects occur at 463, 603, 923 and 1213 K.

The transformations in the activated mixtures occur at lower temperatures (303–323 K). This lowering is most pronounced for the transformations in the temperature range of 553–693 K. A mass reduction of 0.6–3.9% was registered for activated mixtures in the temperature range 313–335 K because of dehydration of the produced $CaSO_4{\cdot}2H_2O$. At temperature of 468 K dehydration occurred of the produced $Ca_3(PO_4)_2{\cdot}xH_2O$, and then, at temperature range 543–598 K, disintegration of $(NH_4)_2SO_4$ to NH_4HSO_4. The mass losses in this range dropped from 12.0% for the non-activated mixture to 7.6% for the mixture treated with chromium–nickel mill balls. This is explained by partial loss of ammonia $(NH_4)_2SO_4$ during the activation of samples and binding of some of the resulting NH_3 and

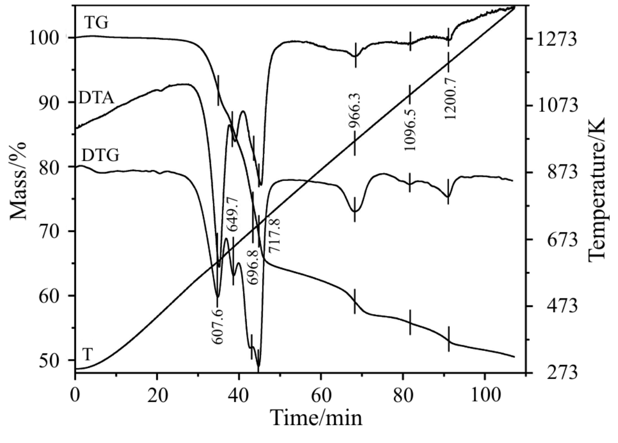

Fig. 2 TG-DTA curves of the initial mixture TF+AS, 1:1

SO_3 into solids in the form of calcium sulphate, ammonia–calcium trimetaphosphate and pyrophosphates. These assumptions are confirmed by the thermal analysis of the non-activated mixture [9] and by the results from the physical methods (Fig. 1 and Table 2). The thermal effects in the temperature range 600–720 K are related to the disintegration of the residual NH_4HSO_4 and to the disintegration of $NH_4CaP_3O_9$ to $Ca(PO_3)_2$ and/or $Ca_2P_2O_7$ [9]. An exothermal and two endothermic peaks were registered in the range 840–950 K with an approximate mass loss of 4.4–6.2%. The first endothermic effect at approximately 840–850 K is missing from the derivatogram of the non-activated mixture (Fig. 2), which is an indication of transformations specific to the activated mixtures.

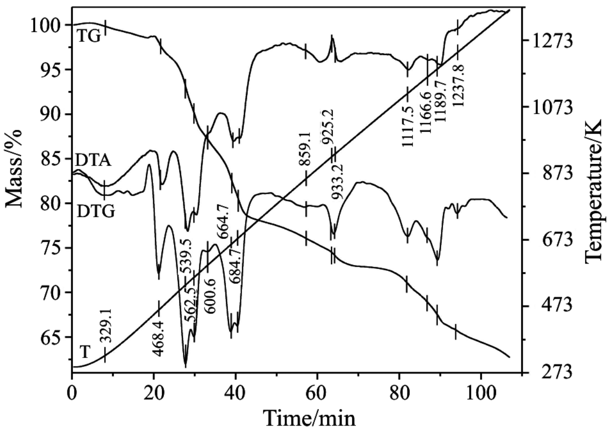

Fig. 4 TG-DTA curves of the mixture TF+AS, 1:1, 10 h in planetary mill, zirconium milling balls

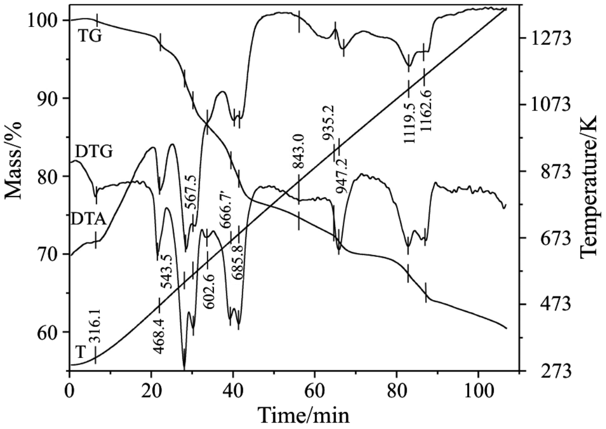

Fig. 3 TG-DTA curves of the mixture TF+AS, 1:1, 10 h in planetary mill, chromium–nickel milling balls

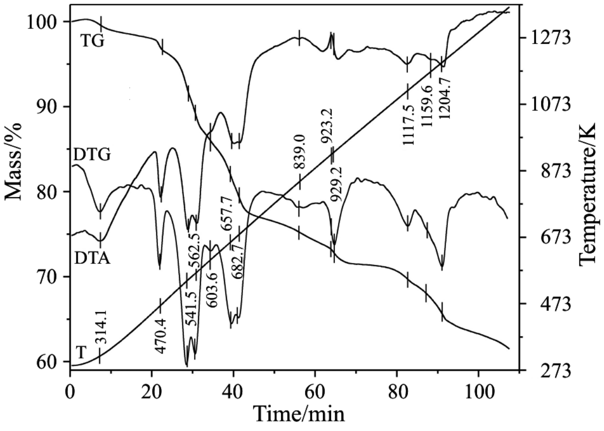

Fig. 5 TG-DTA curves of the mixture TF+AS, 1:1, 10 h in planetary mill, agate milling balls

Table 2 Temperature ranges and mass losses registered at thermal decomposition of TF+AS mixtures activated for 10 h using different mill balls

Stage	Sample/mill balls							
	starting mixture		chromium–nickel		zirconium		agate	
	*T**/K	mass loss/%	*T*/K	mass loss/%	*T*/K	mass loss/%	*T*/K	mass loss/%
I	–	–	316.1	0.87	329.1	0.60	314.1	1.20
II	–	–	468.4	2.31	468.4	2.50	394.4	2.00
III	607.6	11.75	543.5 567.5	5.14 3.51	539.5 562.5	5.40 2.90	541.5 562.5	5.30 3.70
IV	649.7	5.34	602.6	1.67	600.6	1.70	603.6	2.00
V	696.8 717.8	9.92 8.48	666.7 685.8	4.53 4.71	664.7 684.7	4.50 3.40	657.7 682.7	4.60 3.50
VI	966.3	5.39	843.1 935.2 947.2	3.00 3.25	859.1 925.2 933.2	1.70 2.30	839.0 923.2 929.2	1.80 2.60
VII	1096.5 1200.7	2.08 2.96	1119.5 1162.6	3.55 2.62	1117.5 1166.6 1189.7 1237.8	2.90 1.60 2.00 1.10	1117.5 1159.6 1204.7	2.10 2.30 2.60
Total		49.51		42.61		37.20		38.50

*T** – temperature at the point of inflexion

The registered mass losses (1.7–3.0%) are probably due to the transformation of $CaH_2P_2O_7$ into α-$Ca_2P_2O_7$ (reactions (6) or (7)) and alongside the separation of other components from the structure of phosphorite (they are highest in the mixture activated using chromium–nickel mill balls) (Fig. 3, Table 2).

$$CaH_2P_2O_7+Ca_3(PO_4)_2=2Ca_2P_2O_7+H_2O \quad (6)$$

$$CaH_2P_2O_7+CaCO_3=Ca_2P_2O_7+CO_2+H_2O \quad (7)$$

The endothermal effect in the 930–950 K temperature range is typical of the disintegration of the $CaCO_3$ trace, and this process occurred with 5.4% loss in the non-activated mixture. This stage showed reduction of mass loss down to 2.3% in activated mixtures. Obviously, part of the calcium carbonate disintegrates in the activation process or is expended during reaction (7) at temperatures of 470–720 K. According to Chaikina [10], the exothermal effect in the 906–930 K temperature range may be due to changes in the structure of $Ca_3(PO_4)_2$ through absorption of CO_2 and H_2O vapours from the environment, but it is more likely that these are thermal relaxations of activated mixtures. The 1193–1213 K temperature range may allow for reaction (8). This is confirmed by the mass losses in this temperature range that increased from 5.0% for the non-activated mixture to 7.3% for the activated mixtures.

$$Ca_2P_2O_7+CaSO_4=Ca_3(PO_4)_2+SO_2+1/2O_2 \quad (8)$$

The thermal analysis results are characteristic of the changes resulting from mechanical impacts on Tunisia phosphorite and ammonium sulphate mixtures which affect the mass losses and thermal effects occurring in the different temperature ranges. The most substantial changes are those in mechanical activation of the mixtures. The different mill balls did not alter substantially the nature of changes in the mixtures and explain the higher reaction capacity of the studied mixtures and the significantly higher contents of soluble forms of phosphorus. This is grounds for the expectation that new products could be created on this basis with adequate forms and ratios of nutrients such as nitrogen, phosphorus, potash and sulphur.

Conclusions

The new data about the properties and composition of the products of mechanical and chemical activation of Tunisia phosphorite and ammonium sulphate using different mill balls show that more diverse phase composition is possible, including ammonia and calcium poly- and pyrophosphates. Increasing the mixture treatment temperature may increase the degree of transformation of non-absorbable forms of phosphorus into absorbable forms which identifies the perspectives for further studies in this area of producing fertilizers with the required properties.

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