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THERMOTRIBOCHEMICAL TREATMENT OF LOW GRADE NATURAL PHOSPHATES

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Stability of mineral mixed fertilizers processed by effective mixing and compaction, using extrusion technology, is a subject of this study. As new products there is a need to learn the possible changes in the phase ratios and caking processes during long term storage. 7 samples with different nutrient components ratios are investigated after one year kept in a storage facility without conditioning.

Applying TG-DTA, electron microscopy and X-ray diffraction methods samples are studied, recording thermal effects and mass losses, type of crystal structures and phase content in the sample. On the base of the results obtained the relationships are discussed and conclusions made about the possibility to safety storage and visible application of the new products as fertilizers in the agriculture for nut ratio of different plant. It is confirmed that the investigated samples, produced on the base of low grade phosphates are stable during long term storage and they could be successfully recommended for practical use in agriculture, using traditional or individual method of fertilization.

Keywords: *extruded mixed fertilizers, SEM, TG-DTA, thermal stability, X-ray diffraction studies*

Introduction

Stability of mineral mixed fertilizers by using non acidic methods became attractive direction for utilization and processing of low grade phosphate ores, because they are not suitable for traditional technologies. Positive results for obtaining new fertilizer environmentally friendly products based on waste have been reported by different authors [1–10]. Thermo-tribo-chemical method for treatment of the low grade raw materials became a new promising way for obtaining complex mixed fertilizers, containing available but not obligatory water soluble solid phases of phosphorous compounds. Structure defects, created during activation of solids increases the reactivity of the systems and makes the efficiency higher [1–5]. Energy accumulated during activation process often is released by the time and temperature rises [2, 3, 11]. Relocation process has a topochemical character and it is depending on the number of parameters. No relationships are derived up to now. This is the reason that such systems should be studied individually. Different authors find out those low grade phosphates-ammonium sulphate mixtures as good bases for fertilizer production, applying non traditional ways of processing [3, 6–13]. The ratio between water and citric soluble forms could easily controlled by using the initial acidic and alkaline reaction components. It was reported that partially acidulated phosphates and ammonium sulphate as a by product from E-beam cleaning technology are amount the suitable components and the products obtained have a high agriculture efficiency [14–16]. Such type of fertilizers may supply plants with the main nutrients – nitrogen, phosphorous, sulfur and calcium/so called NPKS fertilizers/ and also needed microelements.

The aim of this paper is to report the results from the stability studies of such new fertilizers, after one year storage under covered, but not conditioned facility, where during the year humidity was between 55–95% and the temperature varied from 253 to 313 K.

Experimental

Raw materials

The new fertilizers, obtained in an industrial scale installation, have been produced; using mixtures with water content 11.6 mass%. Final mixing and compaction by extrusion have been realized under pressure of 0.8 MPa. Obtained tablets (July 2005 in the KIT AGRO JSC) have cylindrical shape, length of 0.05 m and diameter – 0.01, 0.02 and 0.03 m. After compaction the products have been dried at 333 K for reduction of free water to less than 0.6 mass%. Ratio between nutrients and tablets size have been adjusted for individual fertilization of different greens, fruit

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trees etc. As a raw materials milled and partially acidulated Tunisia phosphorite; industrial phosphorous containing solid waste, ammonium sulphate by product from E-beam installation in Maritsa-East-2 thermal power station, technical grade potassium chloride and carbonate were used as a supplier of the main nutrients. Ammonium Sulphate contains 98.1 mass% $(NH_4)_2SO_4$. As an impurities in mass% are as follows: 1.12 NH_4NO_3, 0.38 H_2O, 0.13 H_2SO_4, 0.0004 Cl^-, 0.0006 PO_4^{3-}, 0.012 Fe and 0.0002% others. Sulphates of zinc, iron and copper, ammonium molybdate and boron acid have been added as microelements in quantities less then 0.1 mass%. Tunisia phosphorite/used for sample d-VP-4/contains 29.58 mass% P_2O_5, 48.40 mass% CaO, 6.48 mass% CO_2, 3.58 mass% SO_3, 2.74 mass% F, 1.88 mass% SiO_2, 1.38 mass% Na_2O, 1.07 mass% R_2O_3, 0.07 mass% K_2O, 0.056 mass% Cl and traces of Cd, Pb, Cr, Ni. Partially acidulated Tunisia phosphorite/used for samples e-VP-05 and f-VP-06/contains 36.07 mass% P_2O_5 as a total, half of the phosphorous phases are as water and citric soluble compounds. Industrial waste/used for samples a-VP-4; b-VP-4; c-VP-4/contains in mass%: 24.91 P_2O_{5t}, 14.13 P_2O_{5s} citric soluble, 37.97 CaO, 6.31 S as gypsum and 3.83 CaF_2. Total content of the main nutrients and microelements in the samples used are shown in Table 1.

Methods

Stanton Redcroft thermal analyzer in temperature range 288–1373 K is used for thermal analysis. Heating rate is 10 K min^{-1} and sample's mass 10.00±0.04 mg and air flow rate $8.3\cdot10^{-6}$ m^3 s^{-1}. TUR M 62 X-ray analyzer with CoK_α radiation and Philips PM SEM 515 are also used.

Results and discussion

Visual observation of the studied samples after 1 year storage did not give any indication about shape changes, start of caking process or recrystallization modifications on the surface or inside of the tablets.

Figure 1 presents SEM photos of the samples. Magnification scale is as follows: 3000 times for samples a, b, c and 2000 for samples d and e. It can be seen that in the samples a and b, where gypsum is introduced with the raw material gypsum crystals are compacted in different way. Sample b, where the content of gypsum is about 10 mass% needle shape gypsum crystals like reinforced fibers are between the other crystal phases, when in sample a, where gypsum content is 50% less such needle crystals could not be observed. It seems that part of gypsum is fixed with some other component. Probably it is double salt with ammonium sulphate. When the gypsum exceeds the double salt ratio it exists in a single gypsum needle shape phase. Crystal phases are with different shape and the particles size is mostly between 10–100 μ. So during storage period of all the samples binding forces kept tablets structure stable and kept the same particles size of the components.

Thermal data represent dehydration of gypsum, thermal decomposition of the ammonium sulphate (in all samples) and remaining part of potassium carbonate (only in samples e-VP-5 and f-VP-6) as single phases in the products and polymerization and condensation reactions of some of the phosphate phases. Ammonium nitrate decomposition is not clearly determined, because of overlapping with the other reactions and small quantity of this component. Temperature intervals and the registered mass losses are given in Table 2. TG-DTG-DTA curves (Fig. 2) are very close to the relationships of the products after drying during processing and do not give any indication of changing thermal stability or rate of dehydration or decomposition processes. The main reactions, related to the behavior of ammonium sulphate and phosphorite, are in a good agreement with the results from the tribo-activation of such mixture [7–12].

Because during thermal studies no unusual phenomena for indication of lower stability or high rate decompositions was observed, it could be stated that the new products are suitable for long term storage without need of special precaution measures, related to the safety. It was found very low adsorption of wa-

Table 1 Content of nutrients in the samples studied (mass%)

Sample index	N	P	K	S	Zn	Cu	Fe	Mo	B	Gypsum
a-VP-1	8.0	8.0	12	9.1	0.1	0.1	0.1	–	–	5.4
b-VP-2	8.1	8.1	5.1	10.3	0.12	0.12	0.12	–	0.06	10.2
c-VP-3	10	10	15	11.2	0.15	0.15	0.15	0.05	0.05	6.3
d-VP-4	12.5	6.0	5.4	12.3	0.1	0.1	0.1	–	–	1.1
e-VP-5	12.5	12.5	5.4	12.5	0.1	0.1	0.1	–	0.1	2.3
f-VP-6	12.5	12.5	5.4	12.4	0.16	0.15	0.15	0.05	–	2.1

Table 2 Temperature intervals and mass losses determined from derivatograms for the main process stages of studied samples

Sample	Free water and gypsum dehydration		Ammonium sulfate and ammonium nitrate decomposition		Condensation of phosphates Stage		Decomposition of carbonates		Total mass loss	
	Temperature range/K	Mass loss/%	Temperature range/K	Mass loss/%	Temperature range/K	Mass loss/%	Temperature range/K	Mass loss/%	Temperature range/K	Mass loss/%
a-VP-1	292–392 392–489.1	0.7 5.6	489–565 565–819	14.0 12.8	819–879 879–963 963–1115	1.4 1.3 3.8	1115–1274	3.7	293–1298	46.0
b-VP-2	291–349 349–468	2.5 4.0	469–560 560–817	15.6 19.2	817–985 985–1115	3.7 4.1	1115–1154 1154–1307	1.2 3.6	293–1307	54.2
c-VP-3	290–398 398–483	2.1 6.3	48–561 561–749	14.9 26.6	884–1011	6.2	1092–1248	3.0	293–1302	59.1
d-VP-4	400–485	3.6	485.0–564 565–731	19.0 18.4	731–849 902–970 970–1040	3.9 1.7 2.0	1040–1156	3.2	293–1291	57.2
e-VP-5	395–445 445–495	1.4 4.7	495–549 549–754	10.5 30.1	754–885 885–1039	4.0 5.7	1145–1261	4.3	293–1292	64.9
f-VP-6	396–444 444–484	1.5 3.1	484–549 549–735	12.7 30.9	735–831 900–1047	3.8 4.8	1133–1245	3.6	293–1297	65.8

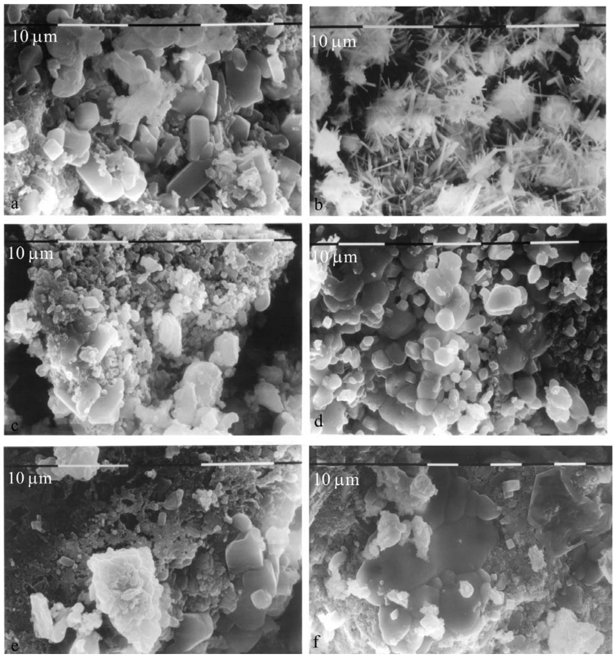

Fig. 1 SEM photos of the studied samples

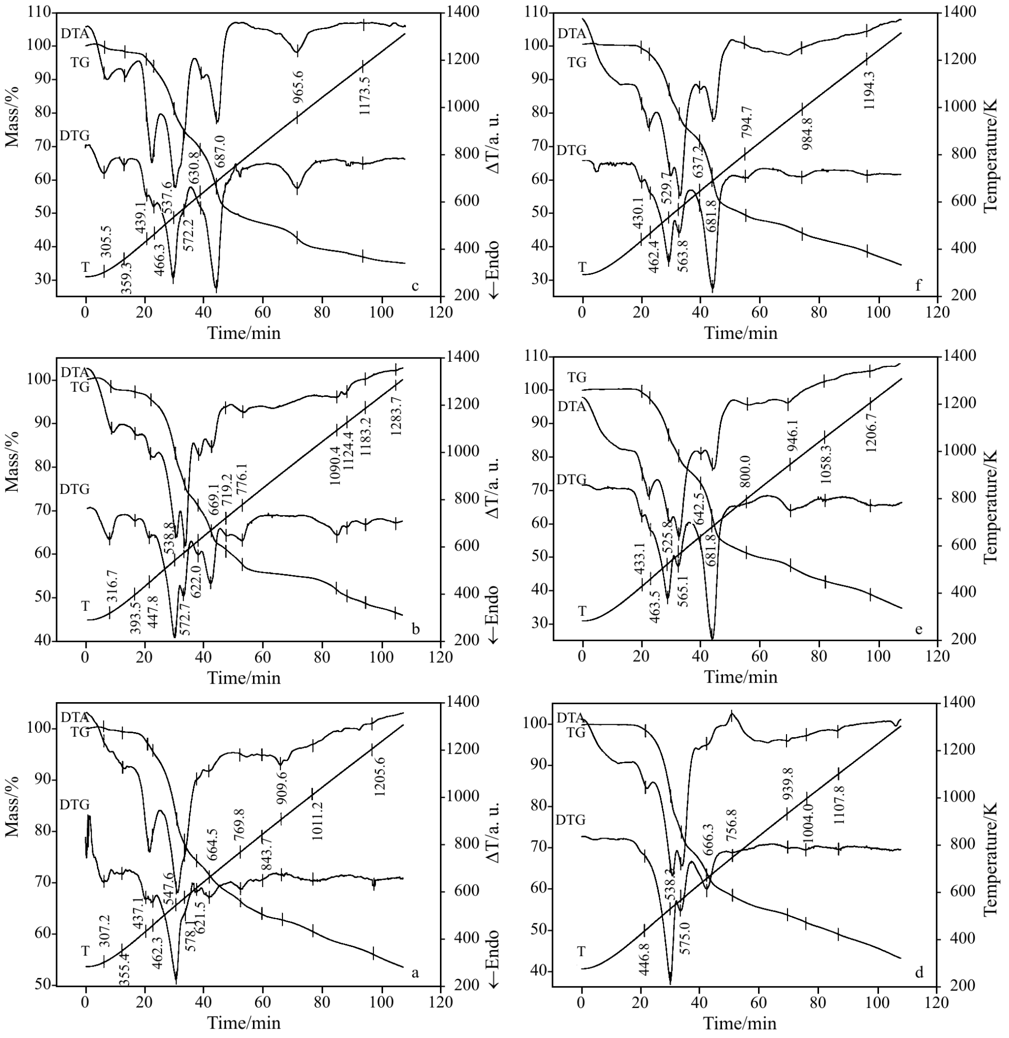

Fig. 2 TG, DTG and DTA curves of the studied samples

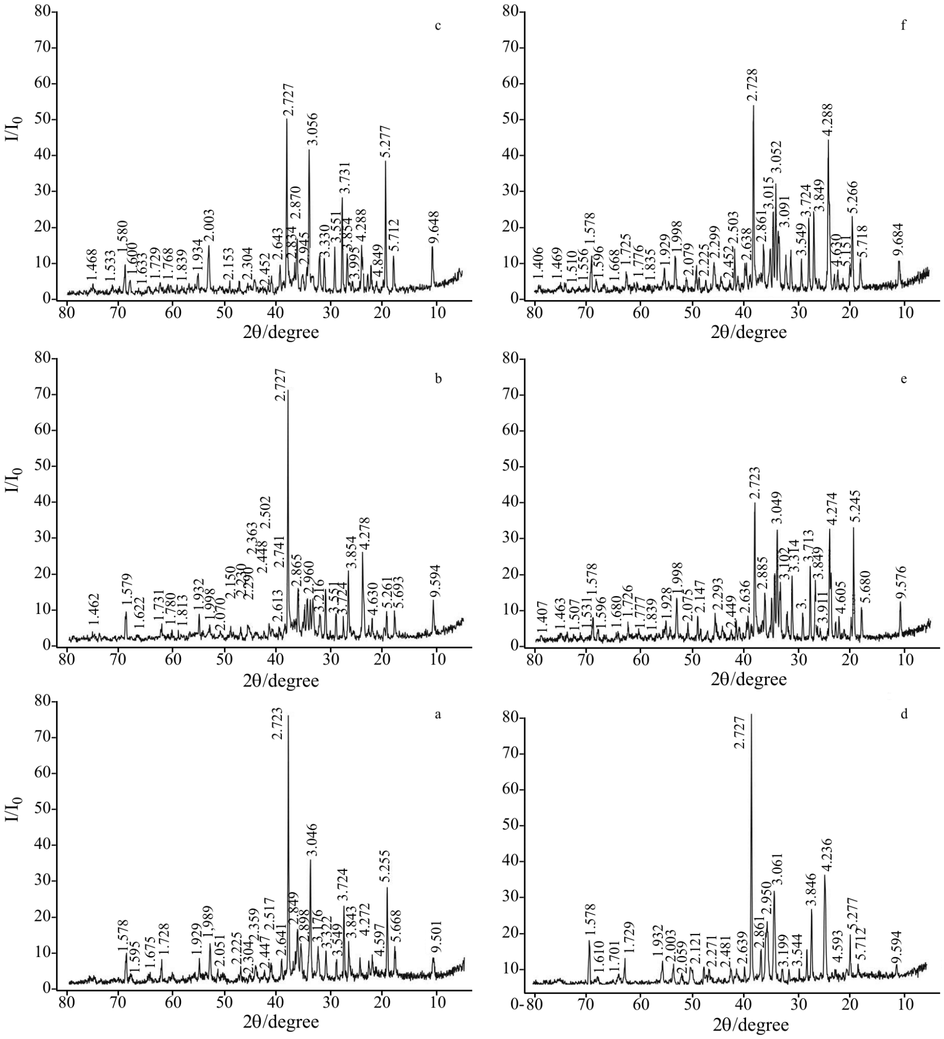

Fig. 3 X-ray diffraction patterns of the studied samples

ter from the atmosphere and the registered free water is in the range of production stage.

Stability of existing solid phases in the products is also confirmed using X-ray diffraction analysis. Diffraction intensities are shown on Fig. 3. As it is expected from the initial compositions of the samples gypsum, ammonium sulphate, silicium dioxide, calcium carbonate and fluorapatite are identified in all samples and potassium carbonate and potassium chloride in samples a-VP-1, b-VP-1, c-VP-1, d-VP-1 and e-VP-1, f-VP-1. $Ca_3(PO_4)_2$, $CaHPO_4$, $CaH_2P_2O_7$, $NH_4H_2HPO_4$, $(NH_4)_2H_2P_2O_7$, NH_4KHPO_4 and K_2SO_4 are registered in the samples as a new phases after thermo-tribo-treatment and compaction process. In samples e-VP-1 and f-VP-1 the presence of β-$CaH_2P_2O_7$ is confirmed. It is obvious that the registered solid phases are result of the proceeding of reactions during treatment of composite fertilizer mixtures during processing. It means that the mechanical and pressure energy introduced during mixing and compaction in the extruder facilitate the chemical reactions between components. As a result the soluble forms of nutrients increase and they are available for plant assimilation. The stability of crystal phases obtained during storage make the products attractive fertilizers and explain the agrochemical efficiency confirmed during some test experiments [13].

Conclusions

New data for structure and thermal stability of new mixed NPKS with microelements fertilizer products after one year storage are obtained. Thermal stability and behavior up to 1273 K confirm that during processing stage different reactions are taking place and formation of new solid phases, like $CaHPO_4$, $CaH_2P_2O_7$, $NH_4H_2HPO_4$, $(NH_4)_2H_2P_2O_7$, NH_4KHPO_4, K_2SO_4, β-$CaH_2P_2O_7$, $CaH_2P_2O_7$, α-$Ca_2P_2O_7$, $NH_4CaP_3O_9$ and $Ca_3(PO_4)_2$, is a fact. That makes the main part of phosphorous from the new products available for plant assimilation. It was found that the crystal structure and thermal stability remain the same after one year storage, without relocation or secondary reactions and it means that there is no need of special precaution measures in the storage facilities, related to the safety working conditions or product quality. The study made is a demonstration how useful could be the thermal investigations in the process of introduction of new chemical products to the market, as it is required by the new chemical legislation.

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