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THERMAL ANALYSIS OF NEW SOIL SORPTION REGULATORS

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Abstract

After mechanochemical treatment of multicomponent mixtures complex fertilizers containing nitrogen, phosphorous, potassium and sulphur (NPKS) with higher water capacity were obtained. As raw materials some solid wastes and ammonia and potassium sulfates were used. Due to the different ratio used, new solid phases in the mixtures are formed. New solid phases are confirmed by the stages and rate of mass changes and also by the thermal effects at different temperature ranges. New phases are also confirmed by using X-ray diffraction method. On the base of data obtained mechanism of chemical transformations is proposed. It was found that the kinetics of mechanical activated mixtures decomposition is significantly influenced by the time of treatment and proceeds in few stages. The results have shown that the soluble nutrients forms ratio and sorption capacity could be controlled by the initial components ratios and treatment conditions.

Keywords: mechanical activation, mixed fertilizers, thermal properties, waste utilization, X-ray diffraction

Introduction

Soil productivity is strongly affected by the way of fertilizing [1, 2]. Using thermo-tribo-chemical method for treatment of raw materials new products could be obtained without generating environmental problems, typical for traditional technologies. The supplied energy helps proceeding of new reactions, increases the reactivity of the systems and makes the efficiency higher [3–11]. Energy accumulated during activation process is often confirmed by thermal analysis [3–5, 11].

Different mixtures have been studied as promising systems for obtaining valuable fertilizers [3–11]. The advantage of such fertilizers is the plants supply with the main nutrients – nitrogen (N), phosphorous (P), potassium (K), sulfur (S) and calcium. By applying follow up compaction of the powdered materials obtained, the rate of nutrients taking up is easy to control [11]. Soil productivity is increasing if the fertilizers could also improve the water capacity of the soils.

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The aim of present work is to apply mechanical activation to the mixtures, containing not only the nutrients, but also a component increasing water capacity of the complex final products.

Methods and raw materials

Different techniques have been applied in the process of the treatment and products properties studies. Retsch Ltd. disintegrator with sieving device 0.1 mm is used for mixing and mechanic activation of the mixtures prepared in advance. Each mixture has an initial mass 0.2 kg. Powders obtained are compacted using hydraulic press at a pressure of 10 MPa. Stanton Redcroft thermal analyzer in temperature range 288–1073 K is used for thermal analysis. Heating rate is the same –10 K min^{-1} and samples mass – 10.0±0.3 mg. Dron X-ray analyzer with CuK_α radiation is also used. Water capacity is determined by conventional weight method.

Solid waste sludge from production of calcium mono-phosphate (food staff grade), ammonium sulfate and potassium sulfate are used as raw materials for nutrients supply and ashes from dust cleaning systems of coal production and thermal power stations (TPS) is used as a sorption capacity improving component. The dry sludge composition is 24.82 mass% P_2O_{5t} (total), 14.23 mass% $P_2O_{5c.a.}$ (citric acid soluble), 0.52 mass% $P_2O_{5w.s.}$ (water soluble); 38.71 mass% CaO, 4.05 mass% F, 6.29 mass% S (mainly as a gypsum), 1.88 mass% SiO_2, 1.07 mass% R_2O_3, 0.07 mass% K_2O, 0.056 mass% Cl. Ammonium sulfate is p.a. grade from Alerus Ltd containing 99.5 mass% $(NH_4)_2SO_4$. As impurities 0.001% NO_3^-, 0.0003% Cl^-, 0.0005% PO_4^{3-}, 0.0002% Fe, 0.00002% As and 0.0002% of other heavy metals are specified by the supplier. Potassium sulfate is also p.a. grade and the content of main compound is 99.29 mass%. The main impurity in it is 0.48% water. The main components of mixed ashes from Maritsa East-1 thermal power station and briquette plant (ME-1B) (without volatile components) in mass% are as follows: 41.30 SiO_2, 16.91 Fe_2O_3, 18.5 Al_2O_3, 8.3 CaO, 4.11 MgO, 1.72 K_2O, 3.91 SO_3.

Results and discussion

The 19 different mixtures were treated and from each of these activated powders 30 tablets with diameter 10 mm have been produced. Contents of the raw materials used in the mixtures are given in Table 1. The selection of the components ratio is on the base of the agrochemical requirements to obtain suitable content of the nutrients and ratio between in the final products.

After 72 h some of the tablets were tested for solubility of the nutrients, static straight and water sorption capacity. It was confirmed that after treatment in all samples nitrogen and potassium were mainly in water-soluble forms. Phosphorous water-soluble forms do not change significantly when the fresh citric acid soluble forms come out and the content of them increases from 56.7 to 85.2–91.7% from the total phosphorous content in the samples. It is clear evidence that during samples' treat-

ment new solid phases are formed and some phosphorous substances are transformed mainly to water-soluble structures. Static straight of the tablets varies from 0.39 to 10 MPa and the water sorption capacity is in the range 15.34-27.64%. Water sorption capacity has the maximum value for sample 1–6. On the way to understand the new solid structures selected samples were studied by using TG-DTA and X-ray diffraction methods. Obtained data are shown on Tables 1–2 and Figs 1–4.

Table 1 Content of the raw materials and properties of the treated mixtures, mass%

No.	$(NH_4)_2SO_4$/ mass%	P_2O_5ws/ mass%	K_2SO_4/ mass%	Ash/ mass%	SS*/ 10^{-1} MPa	SC**/ mass%
1–4	35.42	37.70	10.21	16.67	100.00	15.34
1–6	38.93	27.62	16.79	16.66	65.90	27.64
1–7	25.69	40.94	16.71	16.66	100.00	19.83
1–8	26.71	28.42	11.56	33.31	53.44	18.85
1–9	25.80	34.36	13.95	25.89	78.38	20.98
1–10	32.96	29.23	11.89	25.92	78.38	23.40
1–14	28.70	30.52	14.88	25.92	77.78	20.78

*Static straight; **Sorption capacity

X-ray studies (Figs 1 and 2) of the tablets and ashes confirm the formation of potassium silicate and calcium and ammonium-potassium pyrophosphates as new solid phases. This re-arrangement in the solid phase takes place during mechanic-chemical activation and follow up compaction. It is also associated with re-arrangement of water in the samples, because the changes in both the plasticity of the samples and in wa-

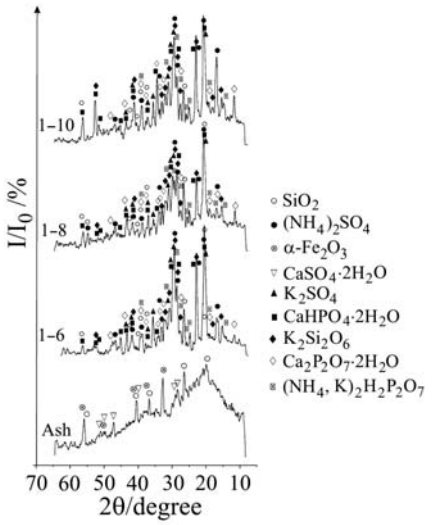

Fig. 1 X-ray diffraction intensities

Table 2 Temperature ranges and observed mass losses for studied samples

Sample	Stage I		Stage II		Stage III	
No.	Temperature range/K	Mass loss/%	Temperature range/K	Mass loss/%	Temperature range/K	Mass loss/%
1–4	298.4–363.1 infl. p.*–326.2	1.1	436.1–497.5 infl. p.–469.7	2.4	542.6–601.6 infl. p.–593.4 601.6–695.1 infl. p.–630.3	8.3 17.5
1–6	 293.4–375.4 infl. p.–313.9	1.3	436.9–501.6 infl. p.–469.7	3.9	501.6–640.2 infl. p.–593.4 640.2–701.6 infl. p.–660.7	17.2 11.7
1–7	292.6–343.4 infl. p.–313.1 343.4–399.2 infl. p.–376.2	1.8 2.4	450.8–477.1 infl. p.–469.7 477.1–508.2 infl. p.–486.9	1.5 1.0	508.2–593.4 infl. p.–582.8 593.4–669.7 infl. p.–612.3	5.4 9.2
1–8	309.8–372.1 infl. p.–335.2	1.8	436.9–500.0 infl. p.–469.7	1.8	529.5–589.3 infl. p.–582.8 589.3–655.7 infl. p.–620.5	5.7 14.7
1–9	292.6–373.0 infl. p.–327.1	2.8	445.1–475.4 infl. p.–468.0 475.4–504.9 infl. p.–489.3	1.5 1.1	504.9–589.3 infl. p.–585.2 589.3–660.7 infl. p.–615.6	5.9 11.6
1–10	291.8–376.2 infl. p.–332.0	3.0	450.8–477.0 infl. p.–473.0 477.0–502.5 infl. p.–486.1	1.0 0.8	502.5–600.0 infl. p.–588.5 600.0–683.6 infl. p.–631.1	8.2 18.3
1–14	304.9–370.5 infl. p.–334.4	2.2	440.2–477.0 infl. p.–468.0 477.0–500.0 infl. p.–485.2	1.3 0.8	500.0–606.6 infl. p.–582.8 606.6–667.2 infl. p.–620.5	9.6 12.4
Ash	302.5–418.9 infl. p.–347.5	8.4	–	–		

Table 2 Continued

Sample	Stage IV		Stage V		Stage VI		Total mass loss/%
No.	Temperature range/K	Mass loss/%	Temperature range/K	Mass loss/%	Temperature range/K	Mass loss/%	
1–4	695.1–746.7 infl. p.*–720.5	5.5	746.7–882.7 infl. p.–812.3	9.4	882.7–981.1 infl. p.–913.1	1.5	48.8
1–6	701.6–766.4 infl. p.–740.2	9.6	766.4–852.5 infl. p.–804.1	6.5	852.5–963.9 infl. p.–893.4	2.2	51.4
1–7	669.7–742.6 infl. p.–712.3	6.6	742.6–863.9 infl. p.–804.1	8.7	863.9–968.0 infl. p.–896.7	1.7	39.9
1–8	655.7–714.8 infl. p.–690.2	7.4	714.8–863.1 infl. p.–787.7	16.7	863.1–951.6 infl. p.–890.2	2.1	52.4
1–9	660.7–721.3 infl. p.–701.6	7.3	721.3–866.4 infl. p.–788.5	13.0	866.4–950.0 infl. p.–900.8	1.7	46.7
1–10	683.6–736.1 infl. p.–717.2	6.2	736.1–868.9 infl. p.–809.8	13.3	868.9–951.6 infl. p.–909.8	1.8	54.4
1–14	667.2–726.2 infl. p.– 696.7	7.1	726.2–877.0 infl. p.–798.4	15.4	877.0–950.0 infl. p.–899.2	1.5	52.1
Ash	520.5–750.0 infl. p.–715.6 750.0–912.3 infl. p.–786.1			37.3 32.0	–	–	79.5

ter releasing during TG-DTA studies were observed. Formation of sulfate adducts is also possible, but it is very difficult to confirm by the methods used.

The TG-DTA curves of ashes (Figs 3, 4, Table 1) show that by increasing temperature, mass losses are observed in two temperature intervals. The first one (302.5–418.9 K) is obviously associated with free water releasing and the endothermic effect confirmed also that. Evaporation of some volatile impurities is also possible. The main losses and the large exothermic effect in temperature range 520–912 K is a result of two-step oxidation of organic compounds and carbon from ashes. It

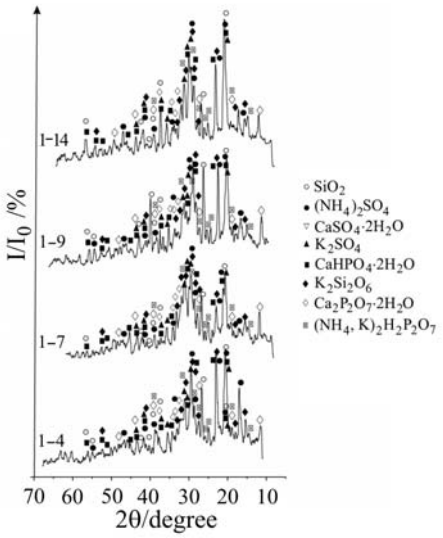

Fig. 2 X-ray diffraction intensities

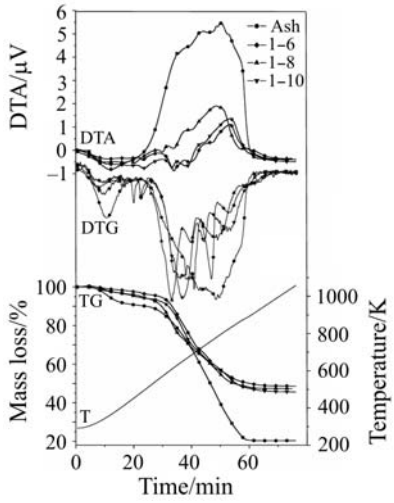

Fig. 3 TG-DTA-DTG curves

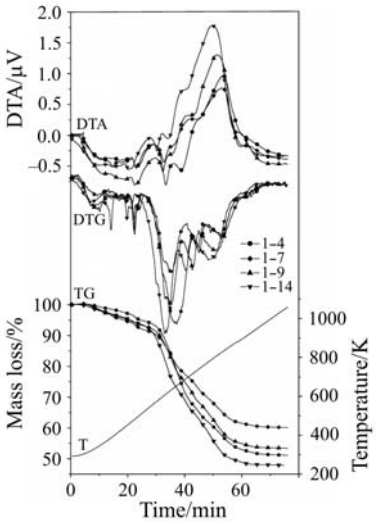

Fig. 4 TG-DTA-DTG curves

should be point out that the content of stable inorganic components (mainly SiO_2 and Fe_2O_3), as it is confirmed from X-ray intensities, are only 20.5%. This explains the high sorption capacity observed for studied samples.

The thermal behavior of the new products characterizes the individual properties of the main raw components, but it is more complicate and indicates new interactions related to the new solid phases and dehydrations. It is obvious that the process is a multistage and it includes various reactions taking place when the temperature increases. The first stage thermogravimetric changes represent the free water releasing (from 1.1 to 3%) and it is followed up by the dehydration of gypsum component (two steps as it is well known). The stages are related to the decomposition of the ammonium sulfate component and as it was shown in the previous study [10, 11] it is 3 stages decomposition process. Mass losses and endothermic effects determined correspond well with the changes of the ratio between raw materials used. Higher temperature range changes (660–981 K) are new thermal effects typical for dehydration and condensation of phosphorous salts formed. The total mass losses vary from 39.9 to 54.4% and it is in a good correlation with the content of volatile part of ashes and water and ammonia content in the other raw materials used. Total mass losses are control mostly by the content of ammonium sulfate and ash in the initial mixture and the minimum value is 39.9% (sample 1–7). Maximum total mass losses are 54.4% and then the content of ammonium sulfate and ash have their maximum (sample 1–10). In the low temperature range (293–375 K) the most stable are mixtures 1–6 and 1–4, where the content of nitrogen and phosphorous components have their maximum and ash and potassium components are at their minimum content. Taking into account that the NPK ratio and the other properties of the tablets, those samples could be classified as an optimal for fertilization use.

Conclusions

The results obtained confirm that the activation of the complex systems from selected raw materials could be used successfully for synthesis of new products suitable for fertilization and improvement soil structure, water capacity and finally soil productivity. The system selected do not require high temperatures or long time mechanical treatment, because of interactions taking place between system components. Control of the initial raw materials ratio permits obtaining final products with properties complying with EU standards for fertilizers. The optimal content of the initial mixture is in the range 35–39% ammonium sulfate, 27–35% phosphorous solid waste, 11–16% potassium sulfate and 16–20% ash.

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