

THERMAL STABILITY AND PROPERTIES OF NEW NPS-FERTILISERS

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Abstract

New NPS-fertilisers are investigated using TG-DTA systems and other techniques to determine their thermal stability and properties. The main component is ammonium sulphate by-product from clean-up technologies. Acidic reaction of ammonium sulphate (AS) is compensated by adding treated or untreated phosphates. Some samples are additionally mechanochemically activated. Tribochemical effects are confirmed. Distribution and conversion of harmful impurities are also studied. The results clearly show that the histories of components, additional treatment and the initial content of impurities affect the thermal properties of the new fertilisers. The mass component's ratio influences the thermal fertiliser's stability and their solubility. It is shown that the by-product from electron beam technology is the most suitable component, because of high-activity. The results obtained confirmed that TG and DTA techniques could be successfully used for products quality control. Most of the simultaneous TG, DTG and DTA curves may have a practical application for future studies and comparative analysis.

Keywords: ammonium sulphate, fertilisers, phosphates, thermal stability and properties, tribochemical treatment

Introduction

Mixed or complex mineral fertilisers could meet the European Directive requirements for safety and environmentally friendly products much better. At the same time new complex and mixed fertilisers can supply much more nutrients [1-4]. Slow releasing fertilisers are preferable [5-15], to avoid acidification effect of most nitrogen containing fertilisers [16-18]. Mechanochemical way of raw materials processing is becoming more effective and environmentally friendly new technology [19, 20]. Those are the main reasons why several studies and papers dealing with this area were published in the last decade. Deficiency of sulphur became a problem for more than 75 countries, according to UN statistics and supply of this nutrient could be efficient by using new fertilisers with sulphates. Thermal stability and properties are essential to the practical application of similar products.

The aim of this work is to study thermal properties of some new fertilisers and to compare their stability with some standard products.

Experimental

Leitz Thermal Microscopy and MOM Derivatograph 1500D and Shimadzu 31H TG-DTA techniques are used. Open plates platinum crucible with diameter of 10 mm and calcium-zirconium crucible with inner diameter 10 mm and height 15 mm are sample carriers for Shimadzu and MOM equipment, respectively. Sample mass is 50 or 200 mg. Mass changes and thermal effects are indicators of structure and phase transitions of fertiliser components. Microscopic observations confirm melting points. Additionally X-ray diffraction method was applied to learn phase composition of initial products and solid residues.

Fertiliser's samples were produced using thermotribochemical treatment of mixtures, containing natural phosphates, ammonium sulphate with different origin and waste acidic solution from caprolactam (CPL) and methylmethacrylate (MMC) production. As a natural phosphate Tunisian phosphorite is used. Chemical analysis is given in Table 1. Initial size of phosphorite particles is under 0.25 mm. Ammonium sulphate is a by-product from different productions – coke, caprolactam and methylmethacrylate and clean-up of waste gases from thermal power station, using electron beam (EB) technology. Specific impurities of ammonium sulphate with different origin are shown in Table 2. Tribotreatment conditions are described in our previous papers [4, 5]. Mass ratio is constant for any mixture – 10 g of phosphorite and 15 g of ammonium sulphate.

Table 1 Chemical analysis of the natural phosphate (Tunisian phosphorite)

Element	Content/%	Element	Content	Element	Content/g t ⁻¹	Element	Content/g t ⁻¹
Ca	32.53	Fe	0.46%	Cr	174.00	Co	3.40
Na	0.93	Si	2.96%	Cu	47.00	Ad	4.30
Mg	0.38	Al	0.27%	Ni	12.04	Mo	2.90
K	0.003	Se	5.00 g t ⁻¹	Pi	37.70	Be	3.00
Mn	0.004	Ti	0.02%	Ca	9.00	As	225.2
Ba	<0.10	Organic	0.60%	Zn	361.22	Cd	20.40
F	3.90	Sb	492.6 g t ⁻¹	Bi	<14.00	V	53.0

Table 2 Main specific impurities of ammonium sulphate with different origin

Compound	Impurity content/%		
	AS – EB	AS – coke	AS – CPL
(NH ₄) ₂ SO ₄	99.12	97.11	95.06
NH ₄ NO ₃	0.21	–	3.94
H ₂ O	0.05	0.89	0.38
Organ. matter	–	1.24	0.46

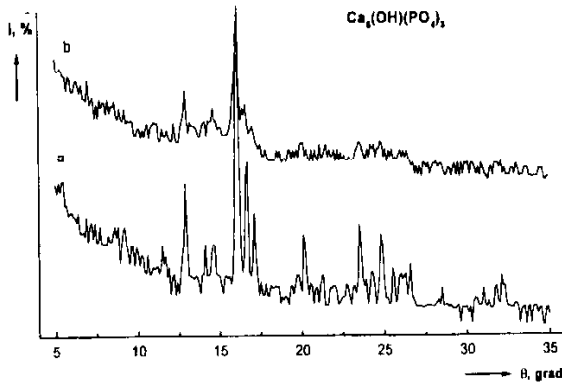


Fig. 1 X-ray diffraction patterns of Tunisian phosphorite; a -- untreated phosphorite; b -- activated phosphorite 20 h in planetary mill

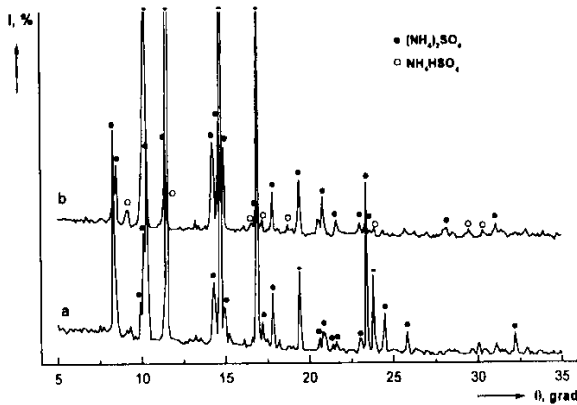


Fig. 2 X-ray diffraction patterns of ammonium sulphate from CPI; a -- untreated phosphorite; b -- activated phosphorite 20 h in planetary mill

Results and discussion

Both raw materials used change partly their crystal structure and composition (Figs 1 and 2) as a result of initial tribotreatment. Hydroxyapatite structure of phosphorite is the most stable one (Fig. 3). At the same time thermal conductivity is affected and the release of volatile organic impurities is higher at lower temperatures for the activated sample. Final mass losses are very close but in the temperature range 810–860 K mass increase is the indicator of the oxidation process. TG, DTG

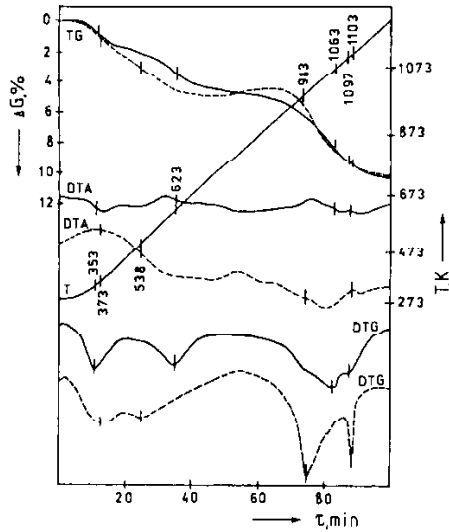


Fig. 3 Simultaneous TG, DTG and DTA curves of Tunisian phosphorite (sample mass 500 mg; S-100 mg; heating rate: 10 K min^{-1}); a – untreated phosphorite; b – activated phosphorite 20 h in planetary mill

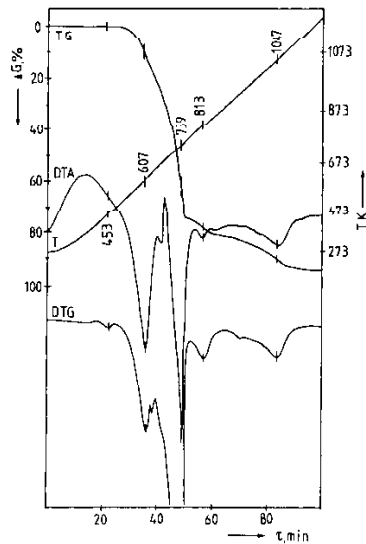


Fig. 4 Simultaneous TG, DTG and DTA curves of untreated ammonium sulphate by-product from CPL (sample mass 200 mg; S-100 mg; heating rate: 10 K min^{-1})

and DTA curves confirm that tribotreatment affect thermal stability and thermal properties in a specific way. The impurities do not play an important role and its origin ammonium sulphate also is partly decomposed during tribotreatment to ammonium bisulphate (Fig. 2). All thermal effects of untreated sulphate are at temperatures between 12 to more than 100 K higher compared to the activated one. The differences are bigger at higher temperatures. At the same time stepwise decomposition is better separated. The areas of all thermal effects for the by-product of caprolactam production are 2–3 times lower for the activated sample (Figs 4, 5) and it confirms that the crystals have much more defects after treatment. It is surprising that tribotreatment does not affect the ammonium sulphate by-product from EB technology, but it should be taken into account that it is a very fine powder and initial particles are in the range of 10–30 microns.

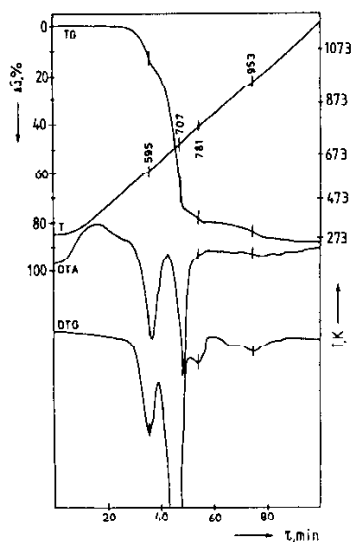


Fig. 5 Simultaneous TG, DTG and DTA curves of activated ammonium sulphate by-product from CPL (sample mass 200 mg; S-100 mg; heating rate: 10 K min^{-1})

Figures 6 and 7 present thermal stability and properties and phase composition of solid residue of untreated and triboactivated mixtures of phosphorite and ammonium sulphate. We observe very different behaviours of the samples. Firstly, total mass losses for the activated sample are higher by almost 8%. Secondly, significant mass changes for the same sample start at very low temperature – at 318 K. Both main steps of mass losses are almost equal to the activated and are closer to straight line. Additionally, much more endothermic effects, well separated, in the temperature range 400–750 K, can be seen. We may assume from this phenomenon that the number of main reactions in that temperature range is higher and it needs further studies to learn more about the chemical mechanism of the process. Using Shimadzu ther-

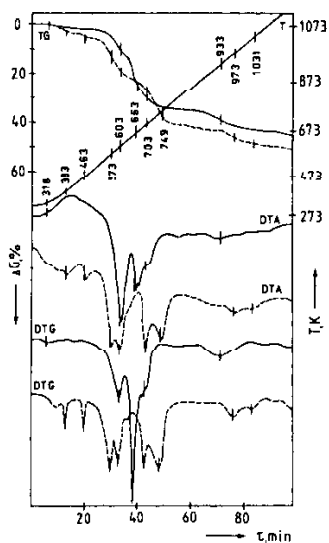


Fig. 6 Simultaneous TG, DTG and DTA curves of CPL ammonium sulphate - Tunisian phosphorite mixture (sample mass 500 mg; S-100 mg; heating rate: 10 K min^{-1}); a - untreated mixture; b - activated mixture 20 h in planetary mill

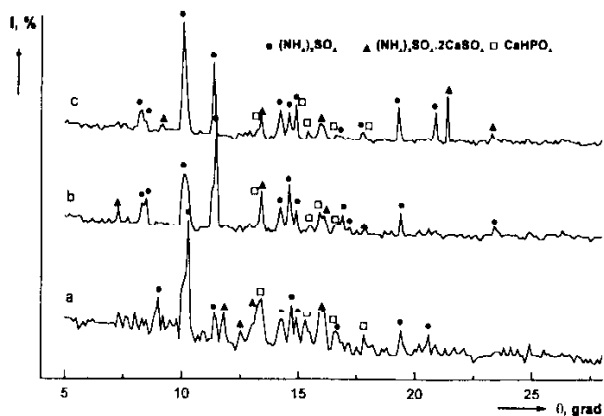


Fig. 7 X-ray diffraction patterns of solid residue from Tunisian phosphorite-ammonium sulphate activated mixtures, after thermal treatment at 573 K; a - mixture with ammonium sulphate from EB technology; b - mixture with CPL ammonium sulphate; c - mixture with ammonium sulphate from coke production

mal analyser with 50 mg sample mass confirms that the gas release does not affect the thermal processes. Anyway, the X-ray diffraction patterns of the solid residue confirm that the gas release is a result of the formation of solid phase with different

composition and it is of high importance for the value of solid product as a mineral fertiliser. As a single crystal phases $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)\text{SO}_4 \cdot \text{CaSO}_4$, CaHPO_4 were determined. Standard chemical analysis of solid products obtained after thermal treatment of the activated sample at temperatures 359, 420 and 673 K show after triboactivation that the content of water soluble P_2O_5 is very low – about 1% from the total P_2O_5 but P_2O_5 from plants (citric soluble) is between 60–70%. At 420 K the citric soluble P_2O_5 comes to 72.24% from total P_2O_5 , and at 673 K – to 75.51%. It is obvious that both phase composition and chemical analysis confirm that via suitable thermotribochemical treatment of ammonium sulphate and natural phosphates a valuable slow releasing NPS fertilisers could be obtained. A better N/P ratio was achieved adding necessary quantities of standard urea or ammonium nitrate. Further studies of such mixtures are to be done.

Conclusions

Thermotribochemical studies on thermal stability and properties of phosphorite from Tunisia, ammonium sulphate with different origin and their mixtures have shown that thermal analysis is an effective way to investigate new NPS fertilisers. It was confirmed that the new products are better, because of slow releasing form of P_2O_5 .

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