Journal of Thermal Analysis and Calorimetry, Vol. 82 (2005) 813–817

THERMAL ANALYSIS FOR IDENTIFICATION OF E-BEAM NANOSIZE AMMONIUM SULFATE

V. Petkova[1]*, *Y. Pelovski*[2] *and V. Hristova*[2]

[1]Central Laboratory of Mineralogy and Crystallography, Bulgarian Academy of Sciences, 1113 Sofia, Acad. G. Bonchev Str. Bl. 107, Bulgaria
[2]University of Chemical Technology and Metallurgy; 1756 Sofia 8 Kliment Ohridski Blvd., Bulgaria

Thermal decomposition of nanosize ammonium sulfate obtained as a by-product in a new electron-beam technology cleaning up waste gases from thermal power stations was studied. DTA-TG-DTG curves were used to characterize thermal properties of the new products obtained under different technological conditions. High quality of ammonium sulfate from Merck was used as a reference material. Ammonium sulfate was the main component in all the products and their thermal behavior was similar to that of the reference. Only the solid product obtained with the highest norm of ammonia contained about 3.2% ammonium nitrate. Thermoanalytical methods can successfully be applied for control the quality of the by-products from E-beam desulfurization technology. It was found that the thermal stability of the nanosize ammonium sulfate was the same as that of the reference ammonium sulfate.

Keywords: *ammonium sulfate, electron-beam technology, SEM, thermal properties, XRD*

Introduction

Ammonium sulfate, released as a by-product from different technologies, contains specific impurities, crystal size and structures, affecting its thermal stability and other properties [1–6]. Up to now the main productions, releasing ammonium sulfate as a by-product, are methylmetacrylate and caprolactame productions as well as cleaning systems of waste gases from coke production. Application of the new electron-beam technology (EBT) for the purification of waste gases from industrial installations, mainly thermal power stations, will generate large quantities of ammonium sulfate, containing ammonium nitrate as the main impurity, the latter being less stable than the former. The by-product is usually used as a fertilizer and its thermal stability and properties are important for the application of the by-product as a fertilizer or as a component of the mixed fertilizers [3–7]. Up to now there are no published studies about the thermal behavior of ammonium sulfate obtained from the application of EBT and it is quite understandable, because EBT is a new technology and only little industrial scale installations are in operation. The main efforts were taken to find out the optimal technological parameters to control the processes and to achieve better purification effects [8]. Ammonium sulfate in this process is formed in the gas phase where there is a field of accelerated electrons. The process is very fast and the reaction time is from 5 to 15 s. The ammonium sulfate, collected as a by-product, is a very fine powder. The specific impurity in it is ammonium nitrate and some other micro-components as, for example, heavy metals. Because of the short time of solid phase formation, radiation effect and specific impurities (especially the explosive ammonium nitrate) a reasonable question came out about the stability and properties of this by-product and its possibilities to be used as a nitrogen fertilizer or a component of other mixed fertilizers.

Thermo-chemical decomposition of the by-product, obtained from demonstration electron-beam installation in Maritsa-East 2 thermal power station, using different technological conditions, is the main objective of the present paper. At the same time the study should give evidence that the thermal analysis could be successfully applied for control the quality of the new industrial product, as it was shown for other environmental applications [9, 10].

Materials and methods

Ammonium sulfate, p.a. grade from Merck Ltd. containing 99.5%$_{\mathrm{mass}}$ $(NH_4)_2SO_4$, with impurities of 0.001% NO_3^-, 0.0003% Cl^-, 0.0005% PO_4^{3-}, 0.0002% Fe, 0.00002% As and 0.0002% specified by the supplier as other heavy metals, was used as a reference (Sample 1). The nanosize by-products ammonium sulfate were processed with different norms of ammonia in the electron

---

* Author for correspondence: vilma_bg@yahoo.com

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 Content of components in the studied by-products

Sample No.	Norm of NH_3	NH_4^+/ mass%	NO_3^-/ mass%	SO_4^{2-}/ mass%	Others/ppm
2	0.4	26.51	0.08	70.89	963 Zn, 22 Cu, 4 Mo, 3 Cd, 18 Ni, 14 Pb, 5 As
3	0.7	26.91	0.14	71.67	647 Zn, 16 Cu, 2 Mo, 2 Cd, 18 Ni, 8 Pb, 3 As
4	0.9	20.86	2.11	70.38	441 Zn, 3 Cu, 2 Mo, 1 Cd, 14 Ni, 3 Pb, 2 As

beam field. Ammonia was supplied at the level of 0.4, 0.7 and 0.9 from the stoichiometric norm. These samples are labeled 2, 3 and 4, respectively. Analysis of the studied by-products has shown that they contain mainly NH_4^+, NO_3^- and SO_4^{2-} ions in the form of ammonium sulfate and ammonium nitrate (Table 1).

Thermal analysis in the temperature range 288–1373 K was carried out with a Stanton Redcroft thermal analyzer. Heating rate was 10 K min^{-1} and mass of samples was 10.00±0.3 mg. Flow rate of air was $0.83\cdot10^{-6}$ m^3 s^{-1}. DRON X-ray analyzer with CuK_α radiation and scanning electron microscopy (SEM) technique were also applied. PHILIPS PH type SEM 515 electron microscope in a secondary emission mode was used.

Results and discussion

DTA, TG and DTG curves of the reference ammonium sulfate and of ammonium sulfate-by-products with different ammonia norms are shown in Figs 1–4. The different stages of mass loss during the thermal treatment of the reference and nanosize by-products ammonium sulfate are summarized in Table 2. X-ray diffractograms data confirm just the presence of ammonium sulfate in samples 2 and 3 and ammonium sulfate plus ammonium nitrate in sample 4.

The thermal decomposition of the reference ammonium sulfate showed a few stages process (Table 2 and Fig. 1), where the first stage was in the temperature range ≈511–629 K. Ammonium sulfate released NH_3 and as a result NH_4HSO_4 and $(NH_4)_3H(SO_4)_2$ could be formed. In the higher temperature range (≈629–750 K) NH_4HSO_4 might decompose to ammonia, water vapour and sulphur oxides. $(NH_4)_3H(SO_4)_2$ could in part be transformed to $(NH_4)_2S_2O_8$. The residue fully decomposed at a temperature range 913–1033 K, where a new portion of gases evolved. Analysis of the results from TG-DTA curves, X-ray diffraction data and the literature data [11, 12] suggests that the decomposition process of ammonium sulfate could be described by the following reactions.

In the first stage (≈511–629 K) with a mass loss of 17.8%:

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

$$2(NH_4)_2SO_4 = (NH_4)_3H(SO_4)_2+NH_3 \quad (2)$$

In the second stage (≈625–750 K), with a mass loss of 77.6%:

$$(NH_4)_3H(SO_4)_2 = 2NH_4HSO_4+NH_3 \quad (3)$$

$$(NH_4)_3H(SO_4)_2+½O_2 = (NH_4)_2S_2O_8+NH_3+H_2O \quad (4)$$

$$NH_4HSO_4 = NH_3+SO_3+H_2O \quad (5)$$

The experimental mass loss in the first stage was higher than the calculated one and it confirms that reaction (1) was the principal reaction. During this temperature range the impurity of ammonium nitrate also decomposed and possibly reactions (3) and (5) from the second stage also had already begun.

The recorded mass loss of 1% at temperatures above 750 K suggests that reaction (4) was not the dominant one during the second stage of transformations. We assume that limited quantities of $(NH_4)_3H(SO_4)_2$ were transformed to $(NH_4)_2S_2O_8$. At

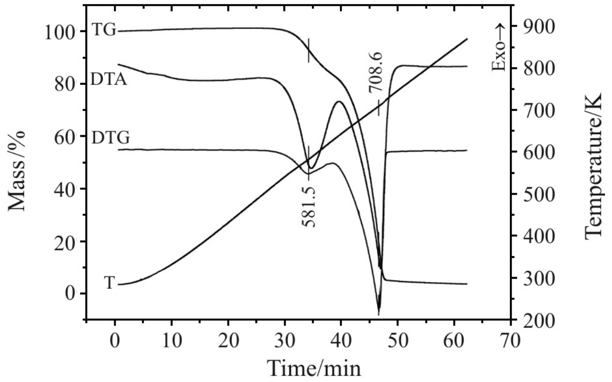

Fig. 1 DTA, TG and DTG curves of Merck p.a. quality ammonium sulfate

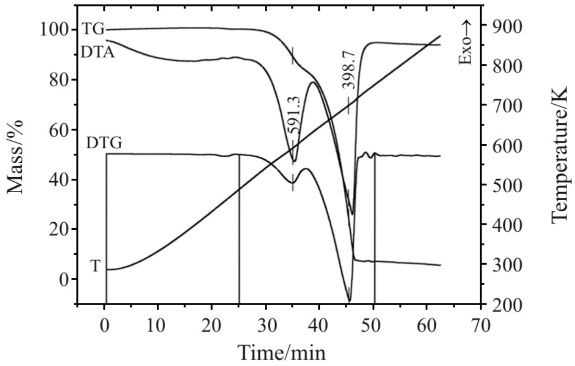

Fig. 2 DTA, TG and DTG curves of ammonium sulfate by-product at 0.4 ammonia norm

Table 2 Mass loss of pure and nanosize by-products ammonium sulfate at different stages of the thermal analysis

Sample No.	Temperature/K			Mass losses/%		Stage's mass losses/%
	Inflection point	Start	End	Start	End	
1	582	511	629	0.0	17.8	17.8
1	709	629	750	17.8	95.4	77.6
1	–	750	1273	95.4	96.4	1.0
2	591	496	616	0.0	16.1	16.1
2	699	616	741	16.1	92.8	76.7
2	–	741	1273	92.8	94.4	1.6
3	590	509	617	0.5	17.2	16.7
3	704	617	752	17.2	95.5	78.3
3	–	753	1273	95.5	96.8	1.3
4	371	339	394	0.5	3.2	2.7
4	595	512	624	4.3	21.5	17.2
4	705	624	744	21.5	99.1	77.6
4	–	744	1273	99.1	99.2	0.1

higher temperatures $(NH_4)_2S_2O_8$ also decomposed, releasing gases, according to reaction 6:

$$(NH_4)_2S_2O_8 = 2NH_3+2SO_3+H_2O+½O_2 \qquad (6)$$

The TG-curves of ammonium sulfate by-product samples (Table 2 and Figs 2–4) confirmed that the mass losses fitted quite well with the above shown mechanism of thermal decomposition of ammonium sulfate and they are in good agreement with the two thermal endo-effects, registered from the DTA-curves. The differences for sample 4 (about 2.7% mass loss and an additional endo-effect recorded at a lower temperature range 339–394 K) are not surprising, because the content of ammonium nitrate in the by-product is higher and the ammonium nitrate is less stable. The decomposition and transformation of ammonium sulfate, according to reactions (1) and (2) for the by-products, started at a little bit higher temperature, but the mass losses were very close to that of the reference ammonium sulfate at this stage. At the second stage of the intermediate decomposition the temperature range and the mass losses were almost the same.

Figure 5 shows SEM micrographs of the reference ammonium sulfate and of ammonium sulfate by-products with different ammonia norms. From the Figure it is obvious that the crystal size in all samples was quite uniform and the shape was not affected by the ammonia norm. On the base of the uniform crystal size we may state that the by-products, obtained from the E-beam installation, were nanoproducts. Thermal stability of the by-products was very similar to the standard ammonium sulfate and from this point of view the by-products covered the requirements for such type of fertilizers. The ammonium nitrate as an impurity, in the studied ranges, did not have significant effect on the thermal stability of the ammonium sulfate.

The chemical analysis confirms that the ammonium sulfate by-products content of nutrients like nitrogen, sulfur, Zn, Cu and Mo were in the range of standard

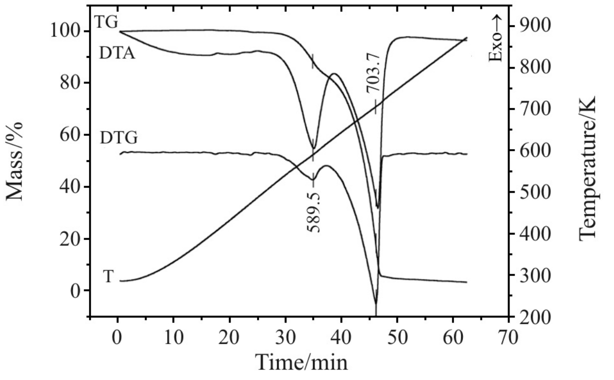

Fig. 3 DTA, TG and DTG curves of ammonium sulfate by-product at 0.7 ammonia norm

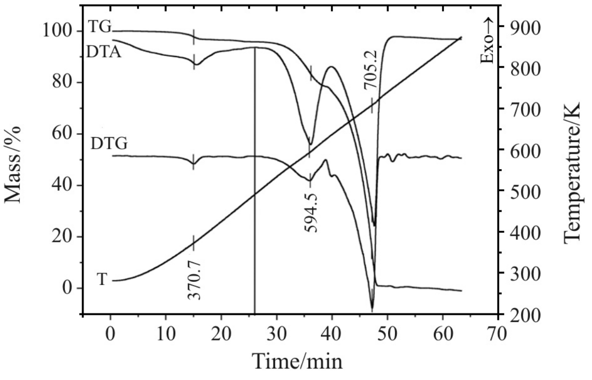

Fig. 4 DTA, TG and DTG curves of ammonium sulfate by-product at 0.9 ammonia norm

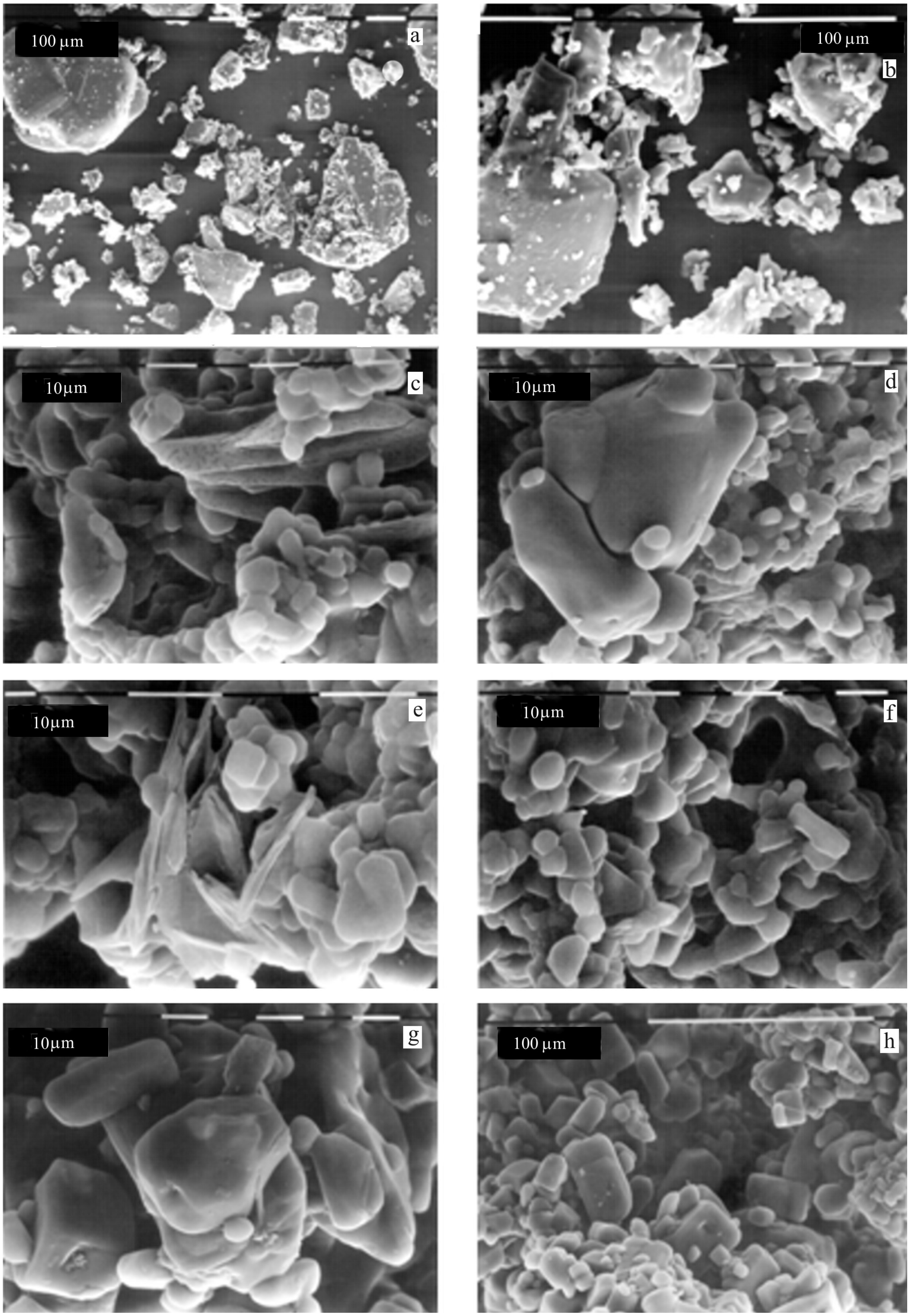

Fig. 5 SEM micrographs of the reference and by-products ammonium sulfate with different norms of ammonia; $(NH_4)_2SO_4$ a – Merck, magnification 100, marker 100 μm; b – Merck, magnification 400, marker 100 μm; c – N=0.4, magnification 1400, marker 10 μm; d – N=0.4, magnification 1000, marker 10 μm; e – N=0.7, magnification 2600, marker 10 μm; f – N=0.7, magnification 1400, marker 10 μm; g – N=0.9, magnification 1300, marker 10 μm; h – N=0.9, magnification 600, marker 100 μm

fertilizers, when the harmful impurities like Cd, Pb, As and Ni were far below the limit values. So it is second evidence that the obtained by-products are environmentally friendly and they can be applied as fertilizers.

Conclusions

New data obtained for the ammonium sulfate by-products, generated from the E-beam installation for cleaning up industrial waste gases from sulfur and nitrogen oxides, could be successfully controlled, using thermal analysis. TG and DTA curves indicate the thermal stability of ammonium sulfate and ammonium nitrate in the by-products. The mass losses registered may be applied for quantitative determination of the mass ratio between them. The results from the thermal analysis of the by-products may also be used to determine the efficiency of the cleaning SO_x–NO_x process.

References

1 Y. Pelovski and V. Petkova, J. Thermal Anal., 43 (1995) 339.
2 M. Veiderma, K. Tonsuaadu, M. Peld and V. Bender, Phosphorus Research Bulletin, 10 (1990) 256
3 M. Arasheva and Jv. Dombalov, J. Thermal Anal., 43 (1995) 359.
4 K. Tonsuaadu, M. Peld, V. Bender and M. Veiderma, J. Therm. Anal. Cal., 56 (1999) 35.
5 I. Dombalov, Y. Pelovski and V. Petkova, J. Therm. Anal. Cal., 56 (1999) 87.
6 Y. Pelovski, V. Petkova and I. Dombalov, J. Therm. Anal. Cal., 72 (2003) 967.
7 K. Tönsuaadu, M. Borissova, V. Bender and J. Pelt, Thermal reactions in synthetic apatite – ammonium sulfate mixture, 'Phosphorus, Sulfur and Silicon', (2004), (in print).
8 Draft Reference Document on Best Available Techniques for Large Combustion Plants, Brussels, European IPPC Bureau, (2001) 146.
9 H. Gehrmann , S. Arvelakis, M. Beckmann and E. G. Koukios, J. Therm. Anal. Cal., 72 (2003) 1019.
10 J. Heikkinen, H. Spliethoff and H. Spliethoff, J. Therm. Anal. Cal., 72 (2003) 1031.
11 L. Erdey, S. Gal and G. Liptay, Talanta, 11 (1964) 913.
12 M. E. Brown, D. Dollimore and A. K. Galway, Reactions in the Solid State, Elsevier Sci., Amsterdam-Oxford-New York, (1980) 223.

DOI: 10.1007/s10973-005-6859-5