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Solid waste management

PROPERTIES OF AMMONIUM SULPHATE FROM MARITZA EAST TPP E-BEAM DESULPHURISATION UNIT

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Abstract. The new desulphurisation facilities of Maritza East-2 TPP generate ammonium sulphate as process by-product. Proper management practice should be applied in order to comply with environmental legislation both for air pollution and waste management. In the present paper the physical, chemical and thermal properties of different ammonium sulphate samples are investigated. Legal basis for its application in agriculture is taken into consideration. Thermal analysis is performed and available solid phases are confirmed by the stages and rate of weight changes and by enthalpy changes at different temperatures. On the basis of the data obtained, speculation on chemical components and transformations in samples are done. Thermal analysis confirms the similarity of ammonium sulphate from desulphurisation facility with pure per analysis grade. The content of nutrients and impurities are determined by using different methods and techniques. Conductivity and pH of water solutions are also determined on the way to assess the potential use of the by-product as fertiliser.

Keywords: ammonium sulphate, thermal analysis, waste utilisation, agriculture.

AIMS AND BACKGROUND

The thermal power plants (TPP) contribute 38% of the national production of electrical energy. Seven coal-fired thermal power plants are operated in Bulgaria. Most of the power capacities (Fig.1) have been commissioned in the mid of 80's, thus their facilities need modernisation in order to comply with environmental protection law. Three trends are obvious in the national energy sector: industrial energy consumption increase, decommissioning of big nuclear power facilities and need of development of local thermal power capacities[1]. However, new changes must be in compliance with the new stricter environmental standards. Very successful step towards air quality improvement has been the commissioning in November 2003 of Electron Beam Irradiation (EBI) Unit for flue gas desulphurisation in one of the biggest thermal power plant in the Balkan peninsula: Maritza East-2 (1450 MW). The pilot scale unit treats 10 000 N m^3/h

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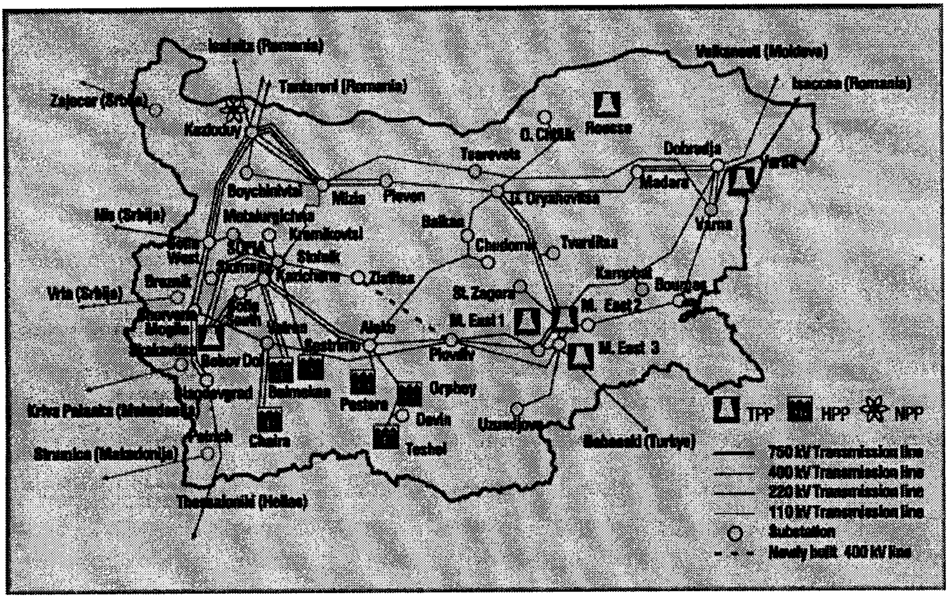

Fig. 1. Electricity production and transfer network in Bulgaria

flue gas and produces about 200 kg/h by-products, major fraction ammonium sulphate.

The present paper investigates the physical, chemical and thermal properties of 9 samples of ammonium sulphate and evaluates opportunities for its land application. This type of utilisation is interpreted in the light of valuable nutrient recycling back in the natural ecosystems.

EXPERIMENTAL

Eight samples of ammonium sulphate (AS-2 to AS-9) have been taken from the new EBI unit during the period 21.11.2003-30.03.2004. The norm of ammonia introduced in the reaction system (α_{NH_3}) is as shown in Table 1.

Table 1. Norm of ammonia introduced (α_{NH_3}) for various samples

Sample	AS-2	AS-3	AS-4	AS-5	AS-6	AS-7	AS-8	AS-9
α_{NH_3}	0.95	0.95	0.95	0.4	0.7	0.7	0.85	0.6

Depending on α_{NH_3}, the contents of ammonium sulphate vary from 97 to 99% and for the higher norms of ammonia 0.5-2% ammonium nitrate is present also. Studies of pH are performed at a 'LP-17' pH-meter and conductivity at a 'CDRV-62' conductivity meter calibrated with 1 M KCl. Thermal analysis is performed at a Stanton Redcroft thermal analyser in temperature range 289-1273 K. Heating rate for all samples is 10 K min^{-1} and samples' mass is 0.100 g. As a control sample (AS-0) ammonium sulphate, p.a. grade was chosen. Its main compound content is 99.5 wt.%. The main impurity is nitrates 0.001 wt.%.

RESULTS AND DISCUSSION

Legal framework analysis. The accession of Bulgaria to the European Union (EU) has required harmonisation of the national legislation with the European[2-5]. All major environment-related laws, together with the IPPC requirements were transposed into the Bulgarian legislation already[4,6]. As a result, national norms require very high standards for environmental protection, including air quality. In respect to this, new flue gas cleaning installations are required to be commissioned.

The BAT guidelines. The relevant reference document on Best Available Techniques (BAT) quotes electron beam irradiation (EBI) as one of 5 main types of combined removal processes together with: solid adsorption/regeneration; gas/solid catalytic operation – at pilot plant stage; alkali injection – at demonstration stage; and wet scrubbing (widely applied for non-large combustion plants)[7]. It is important to underline that EBI is an unique combined removal process because both SO_2 and NO_x are converted to useful by-products – ammonium sulphate and small fractions of ammonium nitrate. According to the scarce data available, until 2003 in the world 4 industrial EBI units are operated – 2 in China, 1 in Poland and 1 in Japan. It is expected that their number will increase due to the beneficial performance proven already.

ANALYSIS OF AMMONIUM SULPHATE FROM E-BEAM IRRADIATION UNIT

Physical and chemical analysis. Solutions of different concentrations were prepared: 2, 4, 6, 8, and 10 g of each sample of ammonium sulphate were diluted up to 250 ml distilled water. Electrical conductivity and pH parameters were measured. When the mass of ammonium sulphate crystals in the solution is increased from 2 to 10 g, then logically the increased ion concentrations lead to decrease in pH value (Table 2) and rise in conductivity (Table 3).

Table 2. Measurements of pH parameter of by-product from EBI unit

Solid/liquid phase ratio	AS-0	AS-2	AS-3	AS-4	AS-5	AS-6	AS-7	AS-8	AS-9
2/250	5.70	5.09	4.19	4.46	4.71	5.60	5.20	4.60	4.13
4/250	5.39	4.66	3.88	4.28	4.66	4.71	4.72	4.36	3.98
4/250	5.30	4.56	3.82	4.08	4.36	4.62	4.60	4.21	3.86
8/250	5.20	5.51	3.80	4.04	4.33	4.45	4.54	4.15	3.82
10/250	5.11	4.40	3.74	4.03	4.29	4.43	4.43	4.09	3.76

Table 3. Measurements of electrical conductivity of by-product from EBI unit, in 10^{-3} S cm^{-1}

Solid/liquid phase ratio	AS-0	AS-2	AS-3	AS-4	AS-5	AS-6	AS-7
2/250	11.63	11.6	11.59	11.35	11.43	11.64	11.41
4/250	21.2	20.5	20.7	20.7	20.5	20.4	20.3
4/250	29.9	29.0	29.2	28.8	29.1	28.6	28.2
8/250	37.7	35.9	36.5	36.9	36.8	37.0	36.9
10/250	45.0	44.2	47.8	47.5	46.7	47.7	44.1

The acidity of the different samples (pH from 5.09 to 4.13) is stronger than the control sample (pH=5.70). This is explained by the availability of strong nitrate ion from ammonium nitrate.

Chemical analysis is performed by an authorised laboratory[8]. The main components (heavy metals) of interest are regulated by the national legislation[9] and are in concentrations as shown in Table 4. Having in mind that the amounts needed for land applications are very low, then exceeding of the maximal allowable concentrations is not probable. Special attention is given to samples AS-9, AS-3 and AS-4 which are the most acidic ones and produce orange-brown precipitate soon after dissolving, probably due to precipitation of iron salts.

Table 4. Chemical analysis of samples of ammonium sulphate sample AS-3

Component	Concentration		MAL in soil at pH= 6.0 (mg/kg dry soil)
	value	unit	
Pb	<3	mg/kg	<70
Cu	7	mg/kg	<120
Zn	963	mg/kg	<200
As	5	mg/kg	25
Cd	<1	mg/kg	1.5
Ni	59	mg/kg	60
Cr	–	mg/kg	190
Hg	–	mg/kg	1

Thermal analysis. Thermal analysis is presented in Table 5. Detailed data about temperature ranges of transformations, relevant inflection points and mass losses are given. The T-TG-DTA curves are compared (Fig. 2) and it is seen that the multistage thermal decomposition has the same character as for pure ammonium sulphate. The ranges of main endothermic effects are very similar and comparable to the reference curve of ammonium sulphate, p.a. grade. No major fluctuations are observed.

Table 5. Temperature ranges and mass loss for samples of ammonium sulphate from EBI unit, 'Maritza East-2' TPP

Sample	I stage		II stage		III stage		IV stage		V stage		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 (%)	
AS-0	291.15-542.15 infl. p.*-461.15	1.0	542.15-672.15 infl. p.-579.15	20.5	672.15-803.15 infl. p. -747.14	80.0	803.15-843.15 infl. p.-826.15	82	–		91
AS-1	291.15-548.15 infl. p.*-383.15	3.5	548.15-675.15 infl. p.*-633.15	24.5	675.15-790.15 infl. p.*-749.15	77.5	–	–	–		94.9
AS-2	291.15-553.15 infl. p.*-409.15	2.0	553.15-703.15 infl. p.*-635.15	20.1	703.15-815.15 infl. p.*-761.15	73.0	815.15-852.15 infl. p.*-833.15	79.0	–		85.7
AS-3	291.15-543.15 infl. p.*-363.15	3.5	543.15-691.15 infl. p.*-626.15	23.0	691.15-804.15 infl. p.*-750.15	80.0	804.15-841.15	81.0	-		94.0
AS-4	291.15-540.15	3.0	540.15-693.15 infl. p.*-639.15	23.0	693.15-803.15 infl. p.*-757.15	78.0	803.15-834.05	79.0	–		89.9
AS-5	291.15-554.15 infl. p.*-381.15	1.5	554.15-693.15 infl. p.*-617.15	21.6	693.15-836.15 infl. p.*-757.15	75.1	–	–	1155.15-1236.15 infl. p.*-1175.15	89.0	92.0
AS-6	291.15-540.15	1.7	540.15-693.15 infl. p.*-619.15	19.5	693.05-812.15 infl. p.*-755.15	75.1	812.15-850.15 infl. p.*-831.15	76.8	1185.15-1231.15 infl. p.*-1197.15 1231.15-1268.15 infl. p.*-1247.15	86.1 86.7	87.5
AS-7	291.15-551.15 infl. p.*-389.15	1.9	551.15-684.15 infl. p.*-631.15	19.7	684.15-813.15 infl. p.*-755.15	75.2	813.15-860.15 infl. p.*-838.15	77.3	–		89.5
AS-8	291.15-539.15 infl. p.*-385.15	0.2	539.15-677.15 infl. p.*-613.15	18.0	677.15-791.15 infl. p.*-735.15	72.3	791.15-837.15 infl. p.*-818.15	74.8	–		85.3
AS-9	291.15-533.15	1.8	533.15-693.15 infl. p.*-627.15	21.0	693.15-821.15 infl. p.*-757.15	78.0	821.15-868.15 infl. p.*-841.15	79.6	–		88.0

* Inflection point.

The process of thermal decomposition could be described as follows:

Stage I	291.15-554.15 K	evaporation of free water molecules
Stage II	533.15-703.15 K	$3\,(NH_4)_2SO_4 = NH_4HSO_4 + (NH_4)_3H(SO_2)_2 + 2\,NH_3$
Stage III	672.15-836.15 K	$(NH_4)_3H(SO_2)_2 = (NH_4)_2S_2O_8 + NH_3 + H_2O$
		$NH_4HSO_4 = SO_3 + NH_3 + H_2O$
Stage IV	791.15-868.15 K	$(NH_4)_2S_2O_8 = 2\,SO_3 + 2\,NH_3 + H_2O + 0.5\,H_2O$
		$SO_3 = SO_2 + 0.5\,H_2O$
Stage V	1155.15-1268.15 K	$(NH_4)_3H(SO_2)_2 = NH_3 + 2SO_2 + 2\,H_2O$

The samples AS-5 and AS-6 show deviation in the temperature range of 1155-1268 K. The two small peaks (Fig. 2) are the result of the final destruction of sulphur compounds.

Samples AS-0 and AS-6 contain weekly bonded water molecules released easily during stage I, while others (AS-3 and AS-8) contain water deeper in their chemical structure and need more energy to release it. The peaks of stage II for

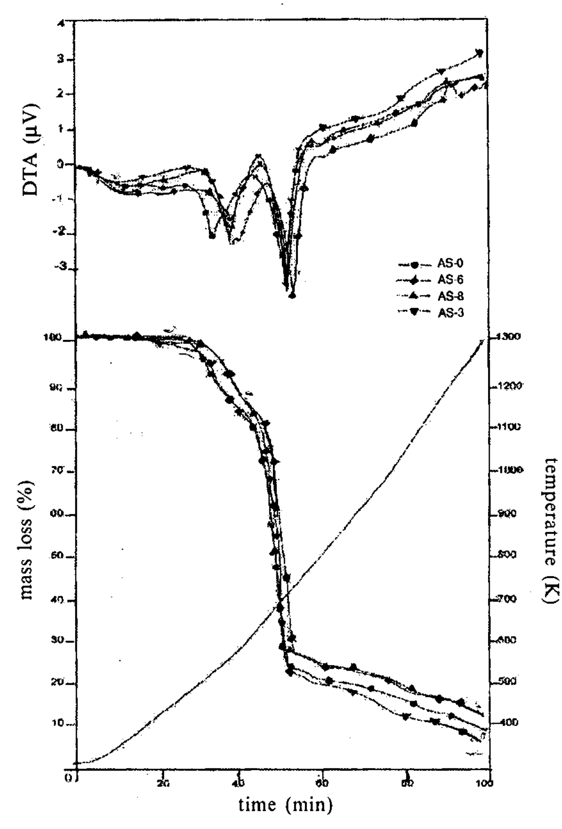

Fig. 2. T-TG-DTA curves for samples of ammonium sulphate from EBI unit

all samples are delayed because of influence of other components, for example ammonium nitrate, even in low quantities. The decomposition of stage III is conducted within very narrow temperature range for all samples. Clear endothermic peak for stage IV exhibit samples AS-0, AS-6, AS-7, AS-8 and AS-9, while for samples AS-2, AS-3 and AS-4 the peaks are not so expressive. The final stage V appears for samples AS-5 and AS-6 only and it is due to the final decomposition of sulphur compounds.

The chemical and thermal properties of the by-product from EBI and ammonium sulphate, p.a. grade are very similar. But because of the specific coal chemical composition, the potential occurrence of varying concentrations of heavy metals is still possible. Therefore, strict compliance with the optimal operational conditions has to be kept and secondary purification processing in order to ensure product suitable for agricultural application.

CONCLUSIONS

In order to improve air quality, new flue gas cleaning facilities must be commissioned in Bulgaria. Good example for successfully operated pilot-scale unit is the electron beam desulphurisation installation at Maritza East-2 TPP. The eight months of test operation have proven its capacity to reduce the emissions to required levels. This fact leads to recommendation for further investigations with respect to capacity expansion.

The chemical and thermal analysis of the by-product generated shows promising possibilities for land restoration and fertilisation purposes. Further practical investigations, for example pot experiments, are recommended to determine most suitable forms and quantities of application.

Having in mind that since the early 1980's the European fertiliser market exhibits trade deficit[10] and the current market is dominated by imported low-cost nitrogen fertilisers, then the option for fertiliser export appears to be viable. During the last decade Bulgaria has been the 5th biggest fertiliser exporter and has chances to reach this level again.

REFERENCES

1. Bulgaria – Electrical Power Generating Equipment, http://www.mac.doc.gov/eebic/Countryr/Bulgaria.
2. National Environmental Strategy and Action Plan 2000-2006, Council of Ministers of Republic of Bulgaria, Sofia, 2001.
3. Environmental Protection Act. State Gazette, issue 91/2002.
4. Waste Management Act. State Gazette, issue 86/2003.
5. Clean Air Act. State Gazette, issue 45/1996.
6. Regulation on Conditions and Procedure for Issuing on Integrated Pollution Prevention Permits

for Commissioning and Operation of New and Operation of Existing Industrial Installations and Facilities. State Gazette, issue 26/2003.
7. Draft Reference Document on Best Available Techniques for Large Combustion Plants, Brussels, European IPPC Bureau, 2001, p.146 and p.150.
8. Protocol No 6.1-033/26.02.2004, Chemical Analysis Results. 'Eurotest-control' Ltd., 2004.
9. Regulation on Admissible Norms for Harmful Substances in the Soil. State Gazette, issue 39/16.04.2002.
10. The Fertilizer Industry of the European Union Data. European Fertilizer Manufacturers Union, Belgium, 1997.

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