NUKLEONIKA 2008;53(Supplement 2):S61–S66

ORIGINAL PAPER

Electron beam flue gas treatment process for purification of exhaust gases with high SO_2 concentrations

Andrzej G. Chmielewski, Janusz Licki

Abstract. Exhaust gases with high SO_2 concentrations are emitted from combustion of high sulphur fossil fuels and from different industrial processes (e.g. copper smelter and sintering plants). The application of the electron beam process for SO_2 and NO_x removal from such flue gases was investigated. A parametric study was carried out to determine the SO_2 and NO_x removal efficiency as a function of temperature and humidity of irradiated gases, absorbed dose and ammonia stoichiometry. The efficiency 90–95% of SO_2 removal was obtained in the optimal treatment conditions with an inlet SO_2 concentration of up to 15% vol. The synergistic effect of high SO_2 content on NO_x removal was indicated. The collected by-product was a mixture of ammonium sulphate and nitrate. The content of heavy metals in the by-products was many times lower than the values accepted for commercial fertilizers.

Key words: high sulphur fossil fuel • flue gas • electron accelerator • SO_2 and NO_x removal efficiency • absorbed dose • by-product

A. G. Chmielewski
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warsaw, Poland

J. Licki✉
Department of Nuclear Energy,
Institute of Atomic Energy,
05-400 Otwock/Świerk, Poland,
Tel.: +48 22 7180144, Fax: +48 22 7793888,
E-mail: licki@cyf.gov.pl

Received: 3 November 2008
Accepted: 2 February 2009

Introduction

Most of the heat and electrical energy worldwide (88%) [1] is produced by the combustion of fossil fuels like coal, natural gas, petroleum, shale oil and bitumen. All of these fuels are composed of major constituents such as carbon, hydrogen and oxygen and other components including sulphur and nitrogen compounds and metals. Unfortunately, the combustion of fossil fuels is not perfectly clean and produces many pollutants that impact air quality, human health, environment and economy as well as contributing to climate change. Most of world's fuels contain excessive amounts of sulphur which is converted to sulphur dioxide when fuel is burnt. Additionally, the combustion process creates various forms of nitrogen oxides. Fuels with sulphur content higher than 1.5% weight are called high sulphur fuels. High sulphur coal is used for power generation in many countries. Sulphur content in Polish hard coal is up to 3.7% weight. There are great resources of high sulphur coal in Spain, England, South Africa, Ukraine and eastern US states. The extensive resources of lignite with sulphur content greater than 2.5% wt. are in the Maritza-East region (Bulgaria), where big thermal power plants are installed. The heavy fuel oils with sulphur content up to 4.0% are used in thermal power plants, refineries, industrial boilers, pulp and paper industry, marine applications and metallurgical operations. Flue gas

Table 1. Main parameters of industrial electron-beam installations

Parameter	Unit	Chengdu TPP, China	Hangzhou TPP, China	Pomorzany EPS, Poland
Flue gas flow rate	Nm^3/h	300,000	305,400	270,000
Inlet flue gas temperature	°C	150	145	140
Inlet SO_2 concentration	mg/Nm^3	5150	2770	2000
Inlet NO_x concentration	mg/Nm^3	820	410	600
SO_2 removal efficiency	%	80	85	90
NO_x removal efficiency	%	18	55	70
Electron beam parameters		800 keV, 320 kWx2	800 keV, 320 kWx2	700 keV, 260 kWx4

emitted from combustion of such fuels contains high SO_2 and NO_x concentrations many times exceeding emission limits, which necessitates the use of add-on control devices for reduction of SO_2 and NO_x emissions. Exhaust gases with high SO_2 concentration up to 15% vol. are emitted from copper smelters and sintering plants [11]. The application of the electron-beam process for purification of such flue gases was the purpose of these experimental investigations. The studies were concentrated on the purification of exhaust gases from combustion of high sulphur coal and heavy fuel oil and from copper smelter. The other aim was determination of the conditions for obtaining the highest SO_2 and NO_x removal efficiencies.

Status of the electron beam flue gas treatment (EBFGT) technology

Electron beam technology is a dry scrubbing process for simultaneous SO_2 and NO_x removal without waste generation. The EBFGT technology was first established in Japan in the early 1970's. This process has since then been investigated from the laboratory scale to pilot and large demonstration scale by research and development projects in Japan, USA, Germany, China and Poland [7]. However, the final engineering design technology for industrial applications was achieved at pilot plants operating in Nagoya, Japan [9] and Kawęczyn, Poland [5]. In the case of the latter new engineering solutions were applied: double-longitudinal gas irradiation, an air curtain separating the secondary window from corrosive flue gases and modifications of the humidification and ammonia injection system (high enthalpy water or steam injection, ammonia water injection). A high dose is required for NO_x removal, while SO_2 can be removed in proper conditions at low energy consumption.

The EBFGT technology for coal-fired boiler has been implemented on industrial scale in the Thermal Power Plants (TPPs) Chengdu [6] and Hangzhou [8] in China and the Electro Power Station (EPS) Pomorzany [4] in Poland. Table 1 presents the main parameters of these installations.

The plants localized in China were designed for SO_2 removal while the Polish installation was designed for simultaneous SO_2 and NO_x removal. The flue gases from two Benson boilers (65 MW (e) and 100 MW (th) each) are purified in the Polish plant (Fig. 1). The maximal

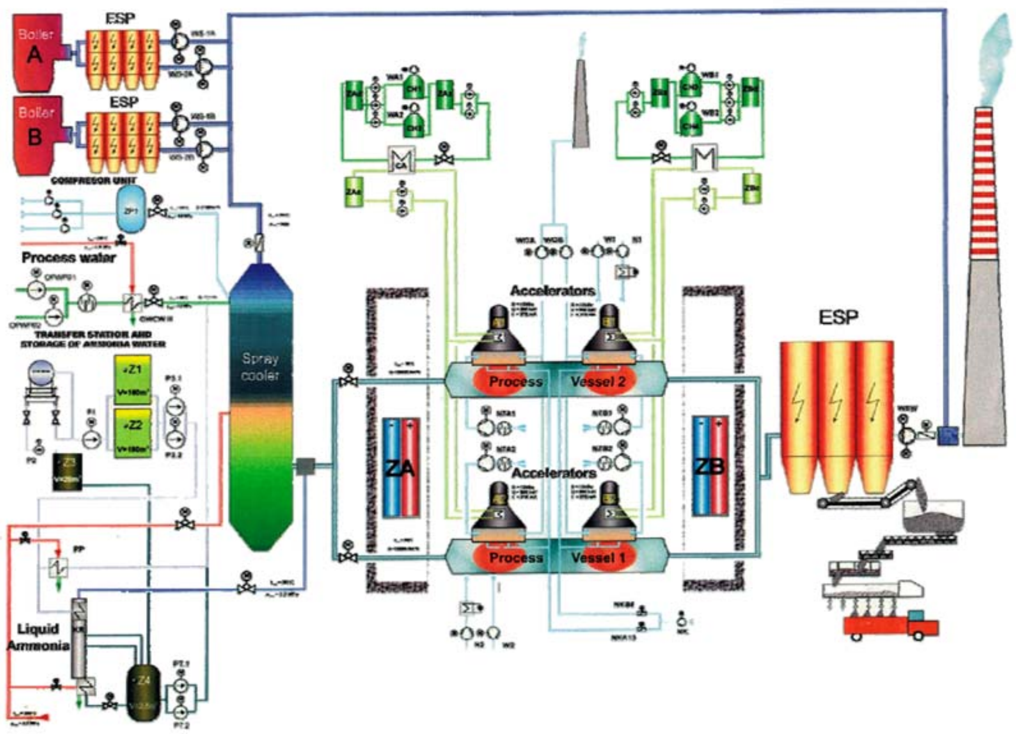

Fig. 1. Technological scheme of the industrial plant at EPS Pomorzany.

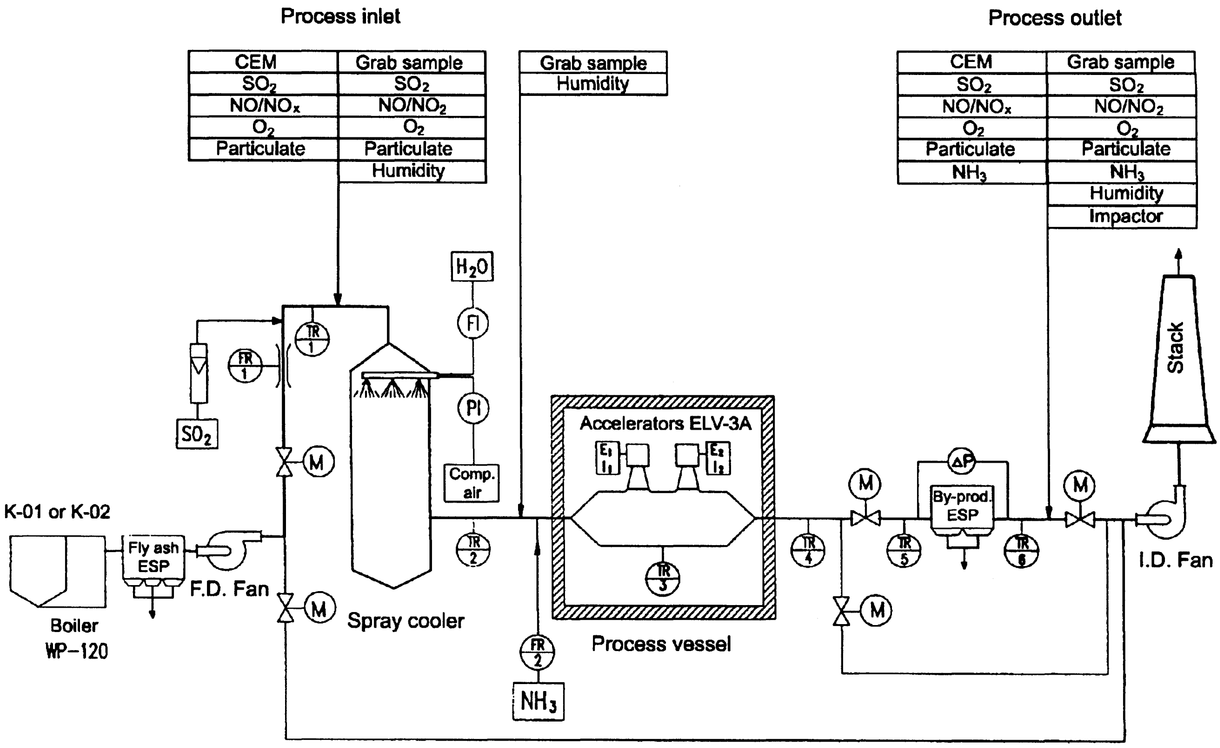

Fig. 2. Schematic flow diagram of the pilot plant at TPP Kawęczyn.

flow rate of the gases is 270,000 Nm^3/h. There are two process vessels over which two electron accelerators (700 keV, 260 kW each) are installed in series. The applied dose is in the range 7–12 kGy. At these doses, the removal efficiency approaches 85–95% for SO_2 and 50–70% for NO_x. The by-product is collected by electrostatic precipitator (ESP) and shipped to a fertilizer plant.

Experimental

Irradiation of exhaust gases with high SO_2 concentration

The study of applicability of EBFGT technology for purification of the exhaust gases with high SO_2 concentrations was performed at two plants.

The pilot plant at the Thermal Power Plant (TPP) Kawęczyn

The pilot plant built at the TPP Kawęczyn was designed for electron beam treatment of flue gas emitted from a coal-fired boiler WP-120 (Fig. 2) [2].

The hard coal with sulphur content about 0.7% wt. was burnt in the boiler and SO_2 concentration in the flue gas was about 500 ppmv. At the pilot plant inlet, the gaseous SO_2 from a cylinder was added in sufficient quantity to the flue gas to increase its SO_2 concentration up to 3200 ppmv. This flue gas with high SO_2 concentrations will simulate exhaust gas from combustion of high sulphur coal with sulphur content up to 4% wt. The study was carried out with flow of 10,000 Nm^3/h of this flue gas, irradiated in the process vessel (PV) by electron beam from two ELV-3A accelerators (700 keV, 50 kW each) (two stage irradiation).

Laboratory plant at the Institute of Nuclear Chemistry and Technology (INCT) in Warsaw

At the INCT laboratory plant, two types of exhaust gases were irradiated by the electron beam from an ILU-6M accelerator (800 keV, 20 kW).

Many thermal power plants combust heavy fuel oil (HFO) – mazout C-3 with 3% wt. sulphur content. The study of application of EBFGT technology for the purification of such exhaust gases was performed at the INCT laboratory plant. For this study, the plant was equipped with a stand for burning of mazout C-3 (Fig. 3).

The applicability of EBFGT technology for the purification of exhaust gases from cooper smelter was tested at the INCT laboratory plant. The study was done with a simulated gas mixture containing the hot gases from gas-fired boiler with an addition of SO_2 and NO_x from the cylinders. The SO_2 concentrations in these mixtures were up to 15% vol.

Analytical system

The reliable and precise measurements of flue gas parameters in crucial points of the plant are necessary for its proper operation and control. Figures 2 and 3 schematically depict the location used for these measurements. Two independent extractive multi-gas monitoring systems were installed to monitor the relevant constituents of the flue gas; one at the process inlet labelled System-1 (upstream of the spray cooler) and the second at the process outlet labelled System-2 (downstream of the ESP or bag filter). Each system consists of:

– SO_2 analyzer Model 40, pulsed fluorescent,

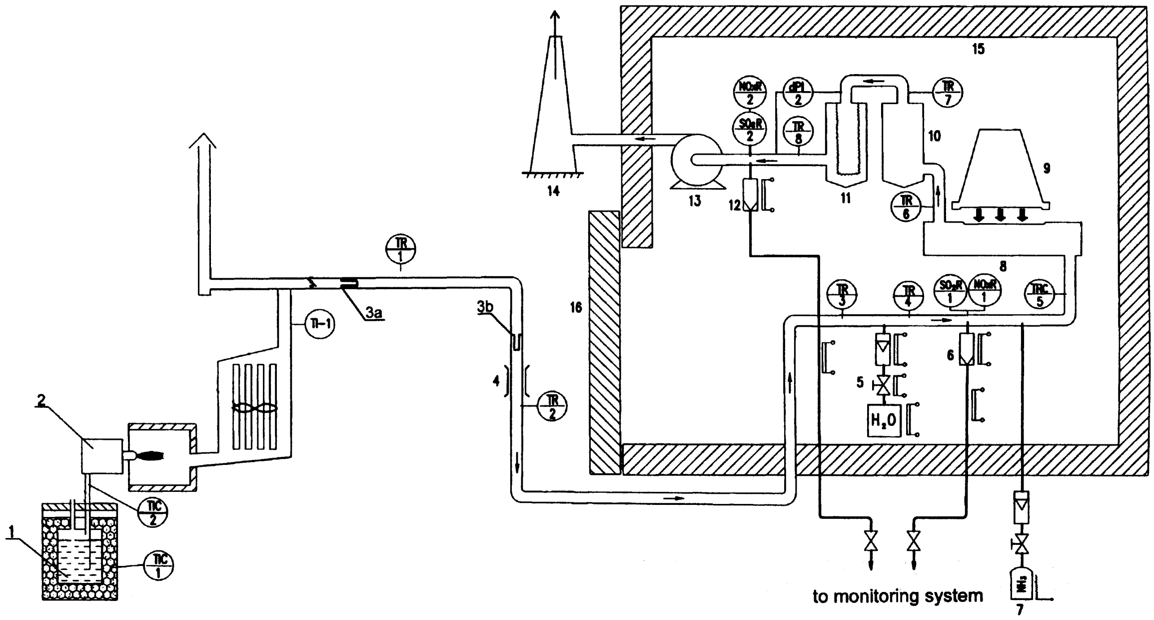

Fig. 3. Flow diagram of the INCT laboratory plant equipped with a stand for burning of mazout C-3. 1 – thermostated fuel oil; 2 – oil burner; 3a – soot filters; 3b – particulate filters; 4 – orifice; 5 – dosage of water vapour; 6 – gas sampling point – process inlet; 7 – ammonia injection; 8 – process vessel; 9 – electron beam accelerator; 10 – retention chamber; 11 – bag filter; 12 – gas sampling point – process outlet; 13 – induced – draught fan; 14 – stack; 15 – concrete shielding wall; 16 – concrete shielding door.

- NO/NO_x analyzer Model 10A/R, chemiluminescent,
- Model 900 for heated sample gas conditioning and dilution. Dilution ratio 20:1 was used.

At the process outlet (System-2), the concentration of unreacted ammonia was determined by a chemiluminescent analyzer Model 17C with two converters. All these gas analyzers were manufactured by the Thermo Environmental Instrument Co. (TEI from the USA). Analyzers readings for SO_2, NO/NO_x and NH_3 were verified using manual analytical methods (grab sample system). The by-product was also analyzed to evaluate its salability as an agricultural fertilizer. An ionic analysis was used yielding the amount of sulphate, nitrate and ammonium ions along with the water and insoluble content.

Result and discussion

In previous studies of this technology it was demonstrated that removal efficiencies of SO_2 and NO_x removal depend on the following process parameters: absorbed dose (D), ammonia stoichiometry (α_{NH_3}) gas temperature at inlet to process vessel (T_{inlet}PV), gas humidity (H) and inlet NO_x concentration (NO_x^0) The parametric studies of SO_2 and NO_x removal efficiency for purification of exhaust gas with high SO_2 concentration were performed at both plants.

Effect of absorbed dose

Figure 4 presents the dose dependence of SO_2 and NO_x removal efficiency. The absorbed dose is a primary factor influencing NO_x removal efficiency. The process starts at zero efficiency for zero dose and indicates saturation at high doses. This demonstrates that NO_x removal is a radiation-induced process. Higher NO_x removal was achieved with a higher absorbed dose. The SO_2 removal is based on two different pathways: thermal process and radiation-induced process. At zero dose, SO_2 removal is caused by the thermal reaction of SO_2 and NH_3 in the presence of moisture. This reaction takes place in the gas phase as well as on the surfaces such as those on the filter cake of bag filter. Sulphur dioxide removal increases sharply with increasing electron beam dose up to 8 kGy and then flattens out at high doses.

Effect of ammonia stoichiometry

The SO_2 removal efficiency increases markedly with increase of ammonia concentration in the irradiated flue gas. Above $\alpha_{NH_3} = 0.9$ this increase is gradual. NO_x

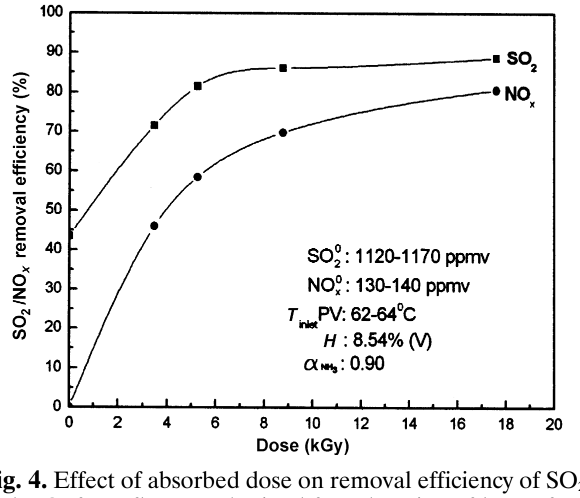

Fig. 4. Effect of absorbed dose on removal efficiency of SO_2 and NO_x from flue gas obtained from burning of heavy fuel oil-mazout C-3.

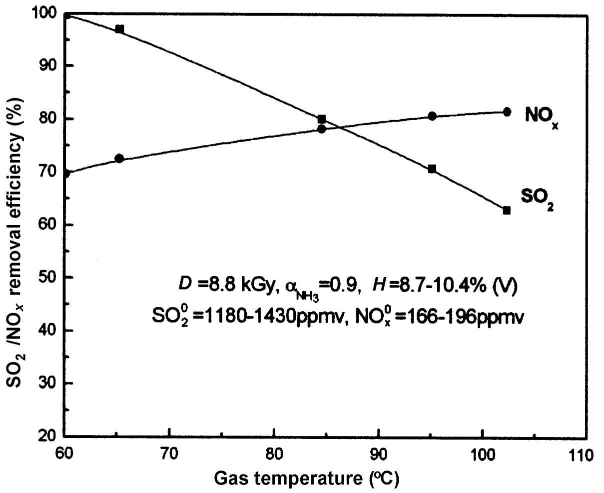

Fig. 5. Effect of gas temperature on NO_x and SO_2 removal efficiencies.

removal efficiency slightly increases with ammonia addition. Fractions of the added NH_3 remain unreacted and exist in the plant outlet (the so-called ammonia slip). In practice, it is desirable to keep the ammonia slip as low as possible due to the environmentally harmful effect of ammonia. In the experiments performed at the pilot plant at the TPP Kawęczyn it was indicated that optimal ammonia stoichiometry should be about 0.9. In this case optimal removal efficiency is obtained for both pollutants as well as slight ammonia slip (lower than 10 ppmv).

Effect of gas temperature at the inlet to process vessel

Figure 5 presents the effect of gas temperature on SO_2 and NO_x removal efficiency. SO_2 removal efficiency strongly increases with lowering gas temperature. This contrasts with NO_x removal which augments with the increase of gas temperature. Gas temperature has a significant impact on the SO_2 removal and a small effect on the NO_x removal efficiency. This indicates that flue gas temperature at the inlet to process vessel can be effectively used to change SO_2 removal efficiency with a minimal impact on the NO_x removal. In the case of flue gas with high SO_2 concentration it is necessary to select low gas temperature in the range 60–70°C to obtain high SO_2 removal efficiency.

Effect of flue gas humidity

The SO_2 removal efficiency increases markedly with the increase of moisture content. This increase is due to the thermal reaction between ammonia and SO_2 without irradiation (thermal reaction). On the other hand, moisture content does not affect removal of NO_x. The optimal removal efficiency of both pollutants is obtained for gas humidity greater than 11% vol.

Effect of inlet high SO_2 concentration

Figure 6 presents the effect of high inlet SO_2 concentration on NO_x removal efficiency. At a given dose

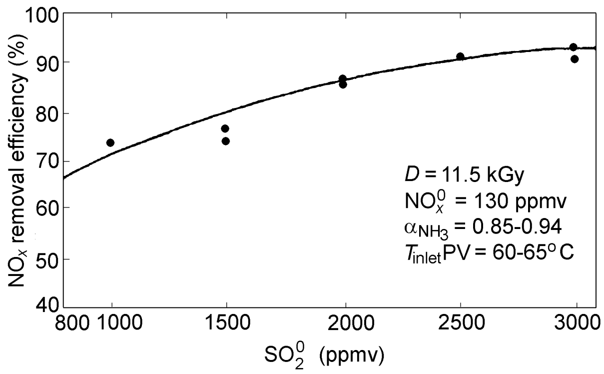

Fig. 6. Effect of inlet high SO_2 concentration on NO_x removal efficiency.

(11.5 kGy in Fig. 6) a definite trend towards improving NO_x removal with increasing high SO_2 concentration was observed. This synergistic effect of high SO_2 concentration is explained by the following radiation induced reaction cycle [10]:

$$SO_2 + {}^{*}OH + M \rightarrow HSO_3 + M$$
$$HSO_3 + O_2 \rightarrow SO_3 + HO_2^{*}$$
$$NO + HO_2^{*} \rightarrow NO_2 + {}^{*}OH$$
$$NO_2 + {}^{*}OH + M \rightarrow HNO_3 + M$$

In the second reaction the HO_2^{*} radical is formed which efficiently oxidizes NO and regenerates the previously spent ${}^{*}OH$ radical. Thus the SO_2 oxidation promotes the NO_x oxidation by generating additional oxidizing radicals. Therefore, the energy consumption of the process is lower for high sulphur flue gas.

By-product

The by-product, collected at the filtration units, was a mixture of ammonium sulphate and nitrate, containing approximately 20% wt. nitrogen as the effective fertilizer component. It can be used either as a single-component fertilizer or as a component of the commercial NPK fertilizer. The content of heavy metals, e.g. [ppm]:

Pb	Cd	Hg	As
< 5	0.5–0.6	0.025–0.05	0.25–0.39

was much lower than the values allowable for commercial fertilizers which are: Pb-140 ppm, Cd-140 ppm, Hg-2 ppm and As-50 ppm.

Conclusions

Flue gases from combustion of high sulphur fossil fuels can be effectively purified by the electron beam process. The SO_2 removal efficiency above 95% and NO_x removal above 75% were obtained in the optimal treatment conditions. High removal efficiencies can be obtained by firstly properly controlling the temperature and humidity of flue gas in a dry bottom spray cooler. Then, a near stoichiometric amount of NH_3 should be added to gas before its inlet to a process vessel. Thirdly, the mixture should be irradiated with adequate irradiation dose in the process vessel. The improvement in NO_x removal is achieved by multi-stage irradiation and by adequate dose distribution between irradiation stages [3]. The gas humidity and temperature, ammonia stoichiometry and irradiation dose up 8 kGy strongly influence SO_2 removal efficiency. The synergistic effect of high SO_2 concentration on NO_x removal was indicated. The collected by-product was the mixture of ammonium sulphate and nitrate. The content of heavy metals in the by-product was many times lower than the values acceptable for commercial fertilizers. In addition, the formation of a valuable product in large quantities might further reduce the operating cost of the EBFGT process depending on the market value of the fertilizer by-product.

Acknowledgment. The paper was supported by the Polish Ministry of Science and Higher Education – project no. PBZ-MEN-3/2/2006 Process engineering for the abatement of harmful and greenhouse gas emissions and their utilization.

References

1. Baukal ChE (2004) Industrial combustion pollution and control. Marcel Dekker Inc, New York-Basel
2. Chmielewski AG, Iller E, Zimek Z, Licki J (1992) Laboratory and industrial research installations for electron beam flue gas treatment. IAEA-SM-325/124. IAEA, Vienna
3. Chmielewski AG, Licki J, Dobrowolski A, Tymiński B, Iller E, Zimek Z (1995) Optimization of energy consumption for NO_x removal in multistage flue gas irradiation process. Radiat Phys Chem 45:1077–1079
4. Chmielewski AG, Licki J, Pawelec A, Tymiński B, Zimek Z (2004) Operational experience of the industrial plant for electron beam flue gas treatment. Radiat Phys Chem 71;1/2:441–444
5. Chmielewski AG, Tymiński B, Licki J, Iller E, Zimek Z, Radzio B (1995) Pilot plant for flue gas treatment – continuous operation tests. Radiat Phys Chem 46:1067–1070
6. Doi Y, Nakanishi I, Konno Y (2000) Operational experience of a commercial scale plant of electron beam purification of flue gas. Radiat Phys Chem 47:495–499
7. Frank NW (1995) Introduction and historical review of electron beam processing for environmental pollution control. Radiat Phys Chem 45:989–1002
8. Mao RJ (2005) Progress of flue gas desulphurization with electron beam irradiation in China. In: Radiation treatment of gaseous and liquid effluents for contaminant removal. IAEA-TECDOC-1473. IAEA, Vienna, pp 45–51
9. Namba H, Tokunaga O, Hashimoto S (1995) Pilot-scale test for electron beam purification of flue gas from coal-combustion boiler. Radiat Phys Chem 46:1103–1106
10. Paur HR (2006) Electron beam scrubbing for high sulphur flue gas. In: Inculet II *et al*. (eds) Modern problems of electrostatics with applications in environment protection. Kluwer Academic Publishers, Dordrecht-Boston-London, pp 111–119
11. Technical assessment of environmental performance and emission reduction options for the base metals (2006) Smelter sector. Final report. Environment Canada