Open Access Journal

Journal of Power Technologies 93 (5) (2013) 330–338

journal homepage:papers.itc.pw.edu.pl

Electron beam technology for multi-pollutant emissions control at a coal-fired boiler, current issues

Janusz Licki[*,a], Andrzej G. Chmielewski[b,c], Andrzej Pawelec[b], Zbigniew Zimek[b], Andrzej Bigos[a]

[a] *National Centre for Nuclear Research, Otwock-swierk, Poland*

[b] *Institute of Nuclear Chemistry and Technology, Warsaw, Poland*

[c] *Warsaw University of Technology, Warsaw, Poland*

Abstract

This review describes current issues concerning electron beam technology for the purification of flue gas from a coal-fired boiler. Fundamental studies of this technology were performed in a pilot plant at Kaweczyn Thermal Power Station. It is a dry scrubbing process ensuring the simultaneous removal of SO_2 and NO_x with high removal efficiency in one step and the generation of a usable byproduct. NO_x removal is performed by a radiation-induced process and its efficiency depends mainly on absorbed dose and inlet NO_x concentration. Higher gas temperature and multistage flue gas irradiation enhance NO_x removal. The synergistic effect of high SO_2 concentration on NO_x removal was observed. The SO_2 removal is based on two pathways: a thermal process (reaction of SO_2 with ammonia in a moist environment) and a radiation-induced process. Its efficiency depends mainly on ammonia stoichiometry and irradiated gas temperature and humidity. SO_2 removal increases sharply as the irradiation dose increases to 8 kGy and then saturation is reached. The byproduct obtained can be used as an agricultural fertilizer or as a component for producing commercial NPK fertilizer. This technology has been already implemented on a full industrial scale at "Pomorzany" EPS. This installation purifies up to 270,000 Nm^3/h of flue gas from two coal-fired Benson boilers. The highest SO_2 removal efficiency obtained reaches 95% while for NO_x it reaches 75%. Two-stage, longitudinal irradiation of flue gas enhances NO_x removal efficiency and reduces energy consumption in the process. During pilot plant operation it was proved that electron beam technology can remove SO_2 and NO_x simultaneously in a wide concentration range of SO_2 (250...3,000 ppmv) and NO_x (140...280 ppmv) with high efficiency. New industrial implementations of this technology have been introduced in China and Bulgaria. This technology is designed for existing plants as a retrofit application as well as for new facilities.

Keywords: coal-fired boiler, flue gas, electron beam, SO_2 removal, NO_x removal

1. Introduction

Coal combustion is the primary means of power generation in Poland, providing 87% of electricity generation. Coal is expected to remain a primary source of energy for at least the next 30 years. However, the combustion of fossil fuels causes the release of various pollutants such as SO_2, NO_x, particulate matter (PM), CO_2, volatile organic compounds (VOCs) and heavy metals, e.g., mercury (Hg), which

*Corresponding author
Email address: j.licki@cyf.gov.pl (Janusz Licki[*,a])

adversely affect human health and harm ecosystems. The emission of these pollutants has been restricted by newly tightened SO_2, NO_x and PM emission limits to reduce pollutant emission and improve the quality of life. Current emission standards under Directive 2001/80/EC demand that electric utilities keep emissions of NO_x and SO_2 below 200 mg/Nm^3, starting in 2016. Most Polish power stations are equipped with electrostatic precipitators (ESPs) for PM control and wet flue gas desulfurization (FGD) systems for SO_2 control. NO_x is mainly controlled by primary methods of NO_x control such as low-NO_x burners and modification of the combustion process [1]. Currently, the primary methods of NO_x control are not sufficient to meet the stringent NO_x limits. Secondary methods of NO_x control such as SCR (selective catalytic reduction) or SNCR (selective noncatalytic reduction) are necessary. Use of a solid-state catalyst requires a higher reaction temperature, additional space and higher operating costs [2]. Catalytic poisoning due to SO_2 laden flue gas is another major drawback, as it reduces the life of the catalyst.

The paper presents electron beam flue gas treatment technology for the purification of flue gas from a coal-fired boiler. It is a dry scrubbing process which ensures simultaneous removal of SO_2 and NO_x with high removal efficiency in one step and the generation of a usable byproduct. In this technology, ammonia is added to flue gas before its inlet to the process vessel (PV) and the gas mixture is then irradiated in the PV by a high-energy electron beam from an accelerator. Basic research concerning this technology was performed in a pilot plant at Kaweczyn Thermal Power Station in Warsaw and it was then implemented on an industrial scale at Pomorzany Electro Power Station in Szczecin. This technology for high-sulfur and high humidity off-gases from low-grade lignite combustion was successfully tested in an industrial pilot plant in Bulgaria. New industrial implementations of this technology have been introduced in China and Bulgaria. The main goal of this paper is to review the current status of this technology.

2. Electron beam flue gas treatment process

Electron beam flue gas treatment (EBFGT) process is a dry scrubbing process for treating pollutants in large-volume atmospheric-pressure exhaust gas streams. In this technology, electrons are accelerated by high voltage in a vacuum region (accelerator) before being injected through thin foil windows to the flue gas in the atmospheric-pressure processing chamber (process vessel). The energetic electrons collide with flue gas molecules and produce reactive free radicals, ions, atoms and secondary electrons that decompose the pollutant molecules in the irradiated flue gases. The main components of coal-fired flue gas are molecules N_2, O_2, H_2O and CO_2. The electron beam energy is absorbed by the flue gas molecules in proportion to their mass fraction. It is consumed in the ionization, excitation and dissociation of the molecules and results in the formation of active free radicals OH, HO_2, atoms O, N and H and ions. These radicals oxidize SO_2 and NO to SO_3 and NO_2 which in reaction with water vapor, present in the flue gas, form H_2SO_4 and HNO_3, respectively. These acids react with added ammonia to form ammonium sulphate and ammonium nitrate. These components are recovered as dry powder inside a particle collector (e.g., ESP). The application of the electron beam technology for the treatment of flue gases from coal-fired power plants has been investigated extensively in both laboratory-and pilot-scale experiments in Japan, the United States, Germany and Poland [3]. In Poland, the fundamental studies into this technology were performed at a pilot plant in Kaweczyn Thermal Power Station in Warsaw ("Kaweczyn pilot plant").

3. Kaweczyn Pilot Plant

The pilot plant was installed on a bypass of the main flue gas stream from the coal-fired WP-120 boiler. The scheme of the installation is given in Fig. 1. Two ELV-3A accelerators (500...700 keV, 50 kW) were installed in series over the process vessel. Flue gas emitted from the boiler is dedusted by an electrostatic precipitator; then one part of it is extracted to the pilot plant and the rest to the stack. In the pilot plant, flue gas passes through an evaporative spray cooler where the gas temperature is lowered

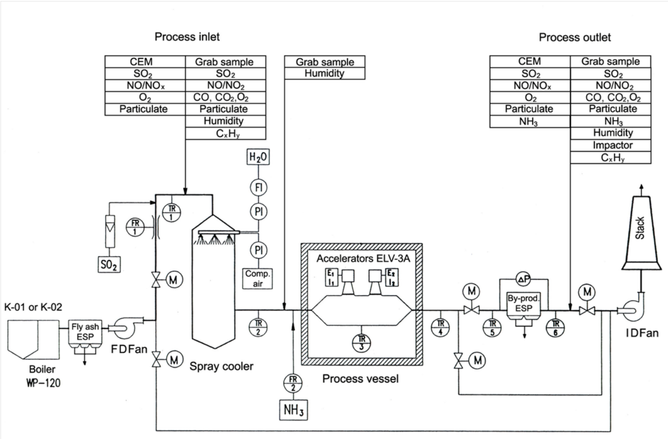

Figure 1: Schematic flow diagram of Kaweczyn pilot plant

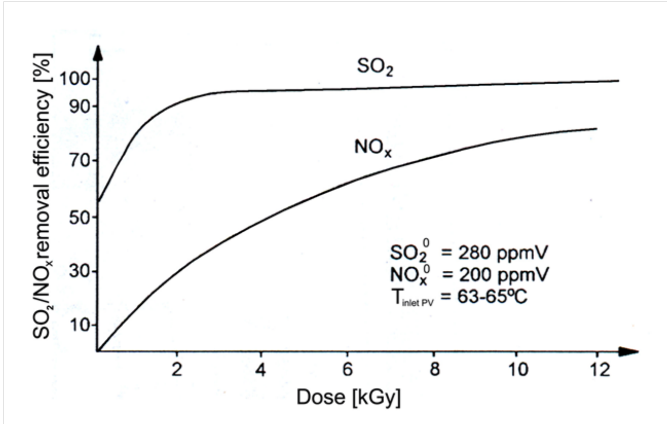

Figure 2: Effect of absorbed dose on the SO_2 and NO_x removal efficiency

as the humidity increases. The near-stoichiometric amount of gaseous ammonia is added to the flue gas upstream of the process vessel. This gas mixture is then irradiated in the PV, which is a 7 m long cylinder with a diameter of 1.6 m. During the electron beam irradiation the SO_2 and NO_x oxidize to form products which subsequently react with added ammonia to form ammonium sulfate and ammonium nitrate. These salts are recovered as a dry powder using a electrostatic precipitator. The collected powder is potentially salable as an agricultural fertilizer. The pilot plant was equipped with a monitoring and control system for reliable and accurate measurements of flue gas parameters at the crucial points of the e-beam installation. Two types of monitoring systems were used to measure gas composition at the process inlet (at the plant inlet) and at the process outlet (at plant outlet): (i) the CEM system - for continuous measurements of SO_2, NO/NO_X, O_2 and particulate concentrations by the gas analyzers systems and (ii) the Grab sample system - for occasional determination of different parameters using manual analytical methods. A detailed description of these systems is given in [4]. Our studies were performed in research cooperation with Japan Atomic Energy Research Institute (JAERI) in Takasaki, Japan, Kernforschungszentrum (KfK) in Karlsruhe, Germany, Ebara International Corporation in Greensburg, USA and the International Atomic Energy Agency (IAEA) in Vienna, Austria.

4. Results and discussion

4.1. Simultaneous SO_2 and NO_x removal. Parametric tests

In the EBFGT process many factors affect the removal of SO_2 and NO_x from flue gas. The main factors are: absorbed dose, ammonia stoichiometry, irradiated gas temperature and humidity, inlet NO_x concentration and inlet SO_2 concentration and configuration of the irradiation system.

4.1.1. Effect of absorbed dose

Absorbed dose is the electron beam energy absorbed per unit mass of irradiated gas. It is expressed in kilograys (1 kGy=1 kJ/kg). Fig. 2 presents the effect of absorbed dose (in short dose) on the simultaneous removal of SO_2 and NO_x . The absorbed dose is a primary factor influencing NO_x removal efficiency. The process started at zero efficiency for zero dose and indicated saturation at high doses. This proves that NO_x removal is a radiation-induced process. A higher dose induces higher NO_x removal.

SO_2 removal is based on two different pathways: a thermal process and a radiation-induced process. At zero dose, SO_2 removal is governed by thermal reaction of SO_2 and NH_3 in a moist environment. This reaction takes place in the gaseous phase as well as on surfaces such as those on the filter cake of the bag filter and the collector plates of the ESP. The yield of the thermal reaction depends on the gas temperature and humidity and decreases as the temperature

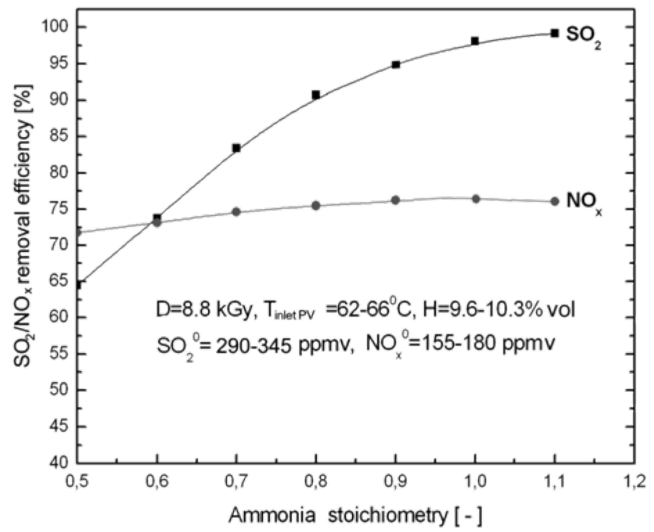

Figure 3: Effect of ammonia stoichiometry on SO_2 and NO_x removal efficiency.

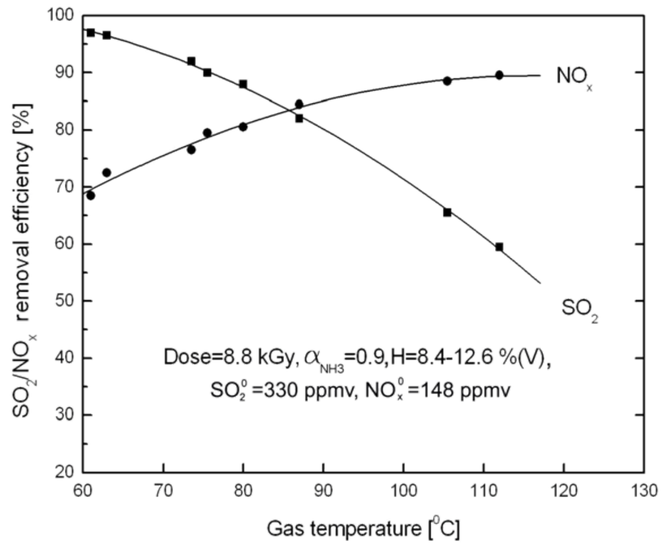

Figure 4: Effect of gas temperature on SO_2 and NO_x removal efficiency

increases. SO_2 removal increases sharply as the irradiation dose increases to 8 kGy, and then a function curve achieves saturation at high doses.

4.1.2. Effect of ammonia stoichiometry

Fig. 3 presents the effect of ammonia stoichiometry. SO_2 removal efficiency increases markedly as the ammonia concentration increases in the irradiated gas. Above α_{NH_3}=0.9 this increase is gradual. The efficiency of NO_x removal increases slightly with NH_3 addition. The fraction of added NH_3 remains unreactive and exits at the plant outlet (the NH_3 slip). In practice, it is desirable to keep the NH_3 slip as low as possible because of its harmful effect on the environment. The optimal NH_3 stoichiometry should be 0.92...0.95. In this case, nearly optimal efficiency of removal was obtained for both pollutants, alongside a slight NH_3 slip (<10 ppmv).

4.1.3. Effect of irradiated gas temperature.

Fig. 4 presents the influence of gas temperature at the PV inlet. NO_x removal efficiency increases moderately with temperature in the range 60...90°C to reach a maximum at 80...90°C. Then it decreases considerably with any temperature rise. This finding is contradictory to SO_2 removal efficiency, which decreases with higher gas temperatures. SO_2 removal efficiency is improved as the gas temperature approaches its dew-point temperature. Gas temperature has a significant impact on SO_2 removal and a small effect on NO_x removal efficiency. This indicates that flue gas temperature at the PV inlet can be effectively used to change SO_2 removal efficiency with a minimal impact on NO_x removal.

4.1.4. Effect of gas humidity.

The flue gas leaving the coal-fired boiler and its ESP has low humidity (5 to 6% (V) by volume). Fig. 5 presents the effect of gas humidity on SO_2 removal efficiency. SO_2 removal efficiency increases markedly as gas humidity increases. This increase is due to the thermal reaction of SO_2 with NH_3 without irradiation. On the other hand, gas humidity does not affect NO_x removal. The optimal removal efficiency of both pollutants was obtained at gas humidity higher than 11% vol. Modification of flue gas humidity and temperature is done in the spray cooler where atomizer water is sprayed into the flowing flue gas. During the water evaporation process gas temperature is decreased and humidity increased.

4.1.5. Effect of inlet NO_x concentration

The influence of inlet NO_x concentration on NO_x removal efficiency was tested by JAERI in the pilot plant at Shin-Nagoya Thermal Power Station in Nagoya (Japan) [5]. Results of this study are presented in Fig. 6.

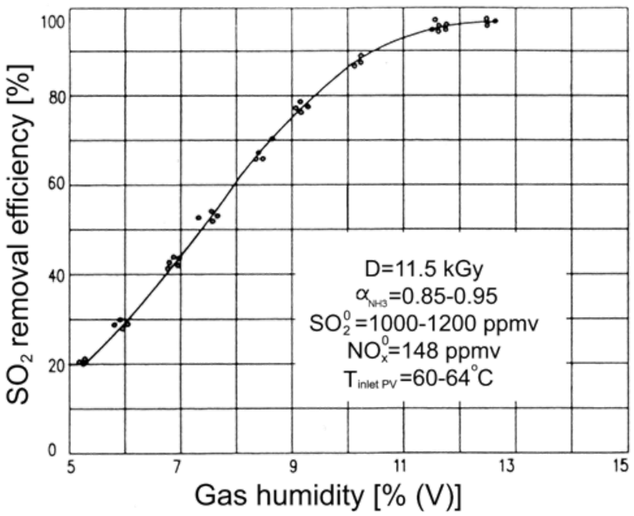

Figure 5: Effect of gas humidity on SO_2 removal efficiency

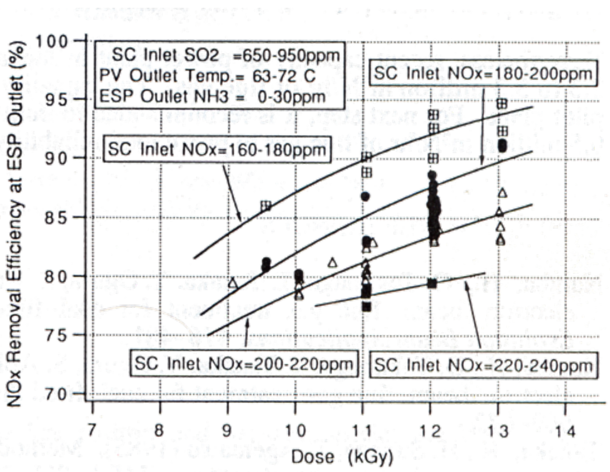

Figure 6: Dose dependence of NO_x removal efficiency at different NO_x concentration [5]

NO_x removal was strongly dependent on inlet NO_x concentration and dose. Higher NO_x removal was achieved with higher absorbed dose and with lower inlet NO_x concentration because the amount of NO_x molecules removed corresponds to the amount of active species formed by electron beam irradiation.

4.1.6. Effect of inlet SO_2 concentration

Polish hard coals contain high amounts of sulfur, in the range 0.5...2.7% by weight, which is converted to sulfur dioxide when burned. SO_2 concentration in flue gas representative of burning high-sulfur coal achieves 3,000 ppmv. The effect of high SO_2 concentration on NO_x and SO_2 removal efficiency was examined in the Kaweczyn pilot plant. The plant uses low-sulfur coal, so flue gases emitted from the WP-120 boiler contain only about 400 ppmv of SO_2. It was necessary to inject the additional amount of gaseous SO_2 from gas cylinders at the inlet to the installation. Fig. 7 presents the results of this test. High inlet SO_2 concentration enhances NO_x removal efficiency. No significant effects were observed on SO_2 removal, which remained at high efficiency levels. This synergistic effect of high SO_2 concentration on NO_x removal can be explained as follows: OH radicals are produced in the irradiated flue gas and play the lead role in simultaneous oxidation of NO and SO_2 to their respective acids.

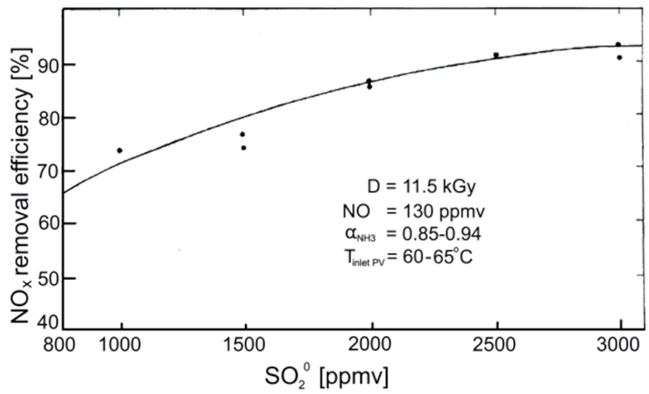

Figure 7: Effect of inlet SO_2 concentration on the NO_x removal efficiency

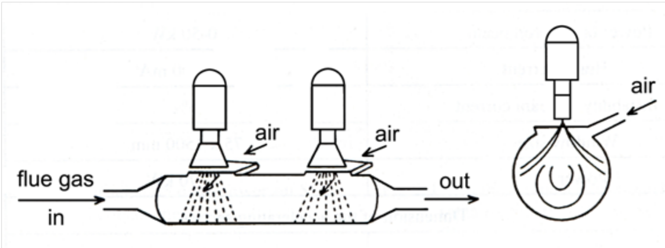

Figure 8: Arrangement scheme of accelerators and process vessel

In the SO_2 oxidation strongly oxidizing HO_2radicals are formed which effectively oxidize NO with regeneration of the previously depleted OH radicals. This test confirms the applicability of the EBFGT process for the treatment of flue gas with a wide range of SO_2 concentration.

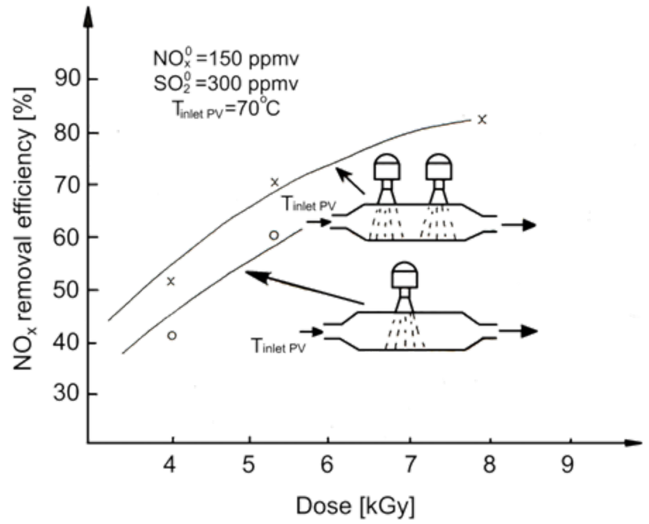

Figure 9: Effect of double irradiation on NO_2 removal efficiency

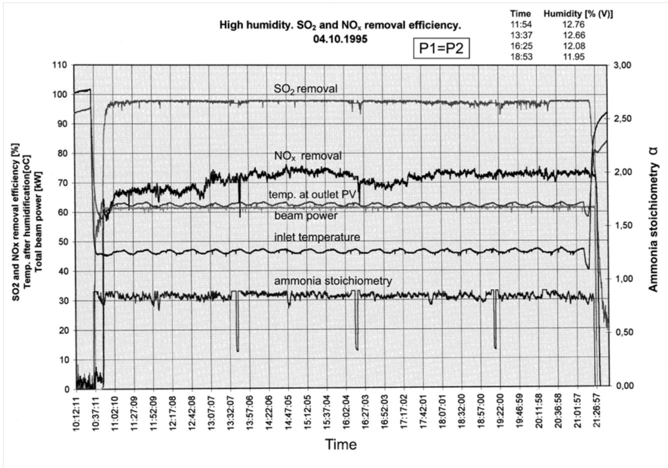

Figure 10: . Records of SO_2 and NO_2 removal during continuous operation tests. Experimental conditions: $SO_2{}^0$—3,000 ppmv, $NO_X{}^0$—165 ppmv, D-12.54 kGy, flue gas flow rate—11,400 Nm^3/h

4.1.7. Effect of configuration of the irradiation system

In the Kaweczyn pilot plant a two step irradiation of the flue gas was first applied (Fig. 8). Two ELV-3A accelerators were installed in series above the process vessel. The process vessel is a horizontal cylinder of diameter 1.6 m and length 7 m. Two windows, made of titanium foil of thickness 50 μm, are located in the wall of the chamber. The outlet-scanning section of the accelerators is located above the surface of the foil. Longitudinal gas irradiation was applied by electron beams. A double window system was applied (the second window being at the outlet of the scanner) and both windows are cooled by an air impingement system. Another important solution was the use of air impingement below the second window. Air impingement below the bottom window secures it against the corrosive action of flue gas. Double irradiation of flue gas achieved higher NO_2 removal efficiency—approximately 20% higher than for a single stage irradiation process (Fig. 9)—and does not affect SO_2 removal efficiency.

One month continuous operation tests were performed at Kaweczyn pilot plant with a wide range of SO_2 concentration (280...3,000 ppmv). The bag filter was used for byproduct collection. Fig. 10 presents an example of a plant performance reading. These tests confirm the applicability of the EBFGT process for the treatment of flue gas with a wide range of SO_2 concentration. The high reliability of all plant components, including both accelerators, was demonstrated in hard industrial conditions The Kaweczyn pilot plant was operated easily with good controllability and durability, and was operated for a long period of time without any serious problems.

4.2. Byproduct application

Aerosols formed in the EBFGT process (ammonium sulfate and nitrate) are captured in the particle collector (e.g., ESP). The size distribution of the aerosols at the outlet of the process vessel in the Kaweczyn pilot plant was determined using an 8-stage Andersen Cascade Impactor. Fig. 11 presents the results of this test. The particles formed are small, with a diameter of less than 1 micron, and sticky. For their capture three types of filter were tested: bag filter, gravel bed filter and electrostatic precipitator. The electrostatic precipitator is recommended for industrial installation.

In principle, the byproduct with small fly ash content (less than 2% by weight) is equivalent to commercial fertilizer-ammonium sulfate.

Due to the final byproduct agricultural applications, the fly ash in the flue gas at the boiler outlet should be removed with high efficiency at ESP (<60 mg/Nm^3). The granulated form has a higher value and can be sold at a better price, so dry granulators are proposed for byproducts final treatment.

Table 1: The content of heavy metals in the byproducts collected in the ESP at Kaweczyn pilot plant

Content of heavy metals, ppmv	Pb	Cd	Cr	Hg	As
Byproducts	<5	0.5...0.6	1...24	0.025...0.05	0.25...0.39
Polish standard for NPK fertilizer	140	140		2	50

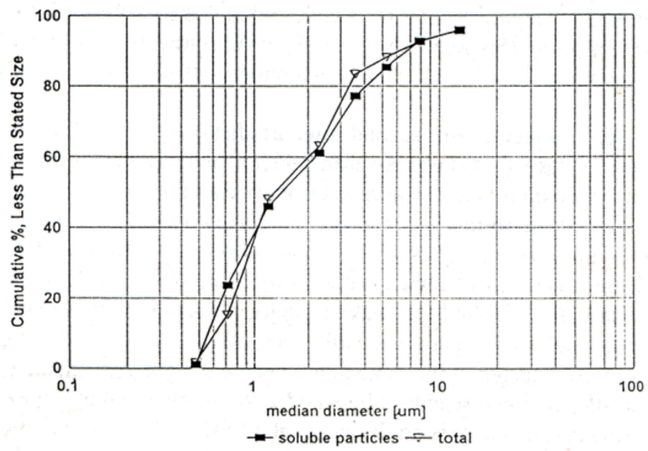

Figure 11: Aerosol particle size distribution in flue gas at the outlet of the process vessel. The experimental conditions: $SO_2{}^0$—3,000 ppmv, $NO_X{}^0$—125 ppmv, D-12.54 kGy, gas humidity—6.52% (V), α_{NH_3}—0.94, flue gas flow rate—6,800 Nm^3/h

The byproducts were officially registered as an agricultural fertilizer in the Japanese Fertilizer Control Act. Another possibility is to use the byproducts as a component of NPK fertilizer. Tests performed in Poland have proved that the blend obtained using e-beam byproduct meets the standards established for this kind of fertilizer. Table 1 presents the content of heavy metals in the byproducts collected in the ESP in tests performed at the Kaweczyn pilot plant.

The content of heavy metals in the byproducts was much lower than the values allowed for commercial NPK fertilizers.

4.3. Industrial implementation of e-beam technology

The positive results of the tests performed on the laboratory-and pilot-plants in Poland, Japan, USA and Germany have led to decisions concerning the design and construction of industrial plant. In Poland, an industrial plant was constructed at Pomorzany EPS in Szczecin. Fig. 12 presents a schematic diagram of the Polish industrial plant. The installation purifies up to 270,000 Nm^3/h of flue gas from two hard coal-fired Benson boilers of 65 MW_e and 100 MW_{th} each. The plant consists of four main parts: a cooling and humidification unit, an ammonia storage and dosage unit, two process vessels and a byproducts collection and storage unit. The flue gas in each process vessel is irradiated by two accelerators (700 keV, 260 kW) installed in series. The byproduct obtained is collected in an electrostatic precipitator and granulated before storage and shipped to the fertilizer plant. The applied dose is in the range of 7...12 kGy. The highest efficiency obtained for SO_2 removal reaches 95%, while for NO_x it reaches 75% [6]. The results obtained during the industrial plant operation confirmed the data obtained during operation of the Kaweczyn pilot plant.

4.4. Bulgarian pilot plant

A pilot plant for electron beam treatment of the flue gas from a lignite-fired boiler was constructed at TPS Maritsa-East 2, Bulgaria. The low-grade lignite with sulphur content of 5.61% wt. (daf) was burnt in the boiler. Flue gas contained a high concentration of SO_2 up to 17,190 mg/Nm^3 and of NO_x up to 220 mg/Nm^3. The flue gases of 10,000 Nm^3/h were irradiated by three high energy accelerators (800 keV, 35 kW). High simultaneous removal efficiency of SO_2 of up to 98% and NO_x of up to 86% were achieved at the low dose of 4 kGy. After successful operation of the pilot plant, the Bulgarian Ministry of Economy and Energy took the decision to use electron beam technology on an industrial scale at Sviloza TPS in Svishtov, Bulgaria. This plant will purify about 600,000 Nm^3/h of flue gas containing high concentrations of SO_2 (2,800...4,800 mg/Nm^3) and NO_x (1,200...1,600 mg/Nm^3).

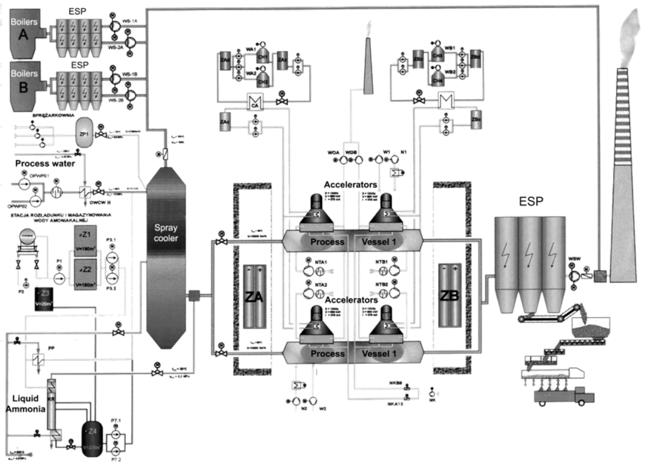

Figure 12: Schematic diagram of the industrial e-beam plant at Pomorzany EPS in Szczecin

5. Conclusion

The tests performed at the Kaweczyn pilot plant proved that electron beam technology provides simultaneous SO_2 and NO_x removal from coal-fired flue gas in a wide concentration range of SO_2 (250...3,000 ppmv) and NO_x (140...280 ppmv), with higher efficiency than the conventional methods. The pilot plant was easily operated with good controllability and durability. It was operated for a long period of time without any serious problems. The byproduct obtained (mainly ammonium sulfate and nitrate) can be used as agricultural fertilizer or as a component for the production of commercial NPK fertilizer. e-beam technology has been already implemented on industrial scale at the coal-fired Pomorzany EPS in Szczecin. Polish industrial plant purifies up to 270,000 Nm^3/h flue gases from two Benson boilers. The highest obtained SO_2 removal efficiency reaches 95% while for NO_x it reaches 75%. The obtained byproduct is collected by electrostatic precipitator and granulated before storage and shipped to the fertilizer plant.

Two-stage, longitudinal irradiation of flue gas was used in the Kaweczyn pilot plant. The scanner of each accelerator was mounted above the secondary window foil in the axis of the process vessel. The electron beam scanned across the gas stream and irradiated the flue gas continuously inside the PV. The diameter of the PV should be adjusted to the penetration range of the electron beam in irradiated gas. The losses in the beam energy delivered to the gas consist of two components: one, the stopping power of two titanium foil windows and the air gap between them and, two, absorption in the walls of the process vessel. For electrons with lower energy, power losses in the windows system are higher and the beam penetrates only a small part of the flue gas in the PV. On the other hand, for higher energy electrons the beam penetrates all the gas in the PV and the rest of its energy is absorbed by the process vessel walls. Therefore, an optimum energy of electron for a given vessel design exists. For the optimum energy, the highest NO_x removal efficiency can be achieved. Further optimization of NO_x removal can be achieved through appropriate dose distribution between the irradiation stages [7]. Optimized use of electron beams through proper arrangement of the irradiation unit increases productivity and reduces unit operation cost.

The long-term Pomorzany industrial plant operation confirmed that the EBFGT process can be dynamically controlled to allow for varying pollutant concentrations and changing flue gas flow rate. With a controlled irradiation dose, flue gas temperature at the PV inlet and an added amount of ammonia, the efficiency of SO_2 and NO_x removal was achieved at a higher level than obtained in commercial methods. This technology is designed for existing coal-fired plant as a retrofit application as well as for new facilities.

References

[1] A. Błaszczuk, W. Nowak, S. Jagodzik, Effects of operating conditions on denox system efficiency in supercritical circulating fluidized bed boiler, Journal of Power Technologies 93 (1) (2013) 1–8.

[2] J. Cwiek, J. Labanowski, M. Sozanska, S. Topolska, Resistance of selected protection coatings to hot corrosion in low-emission coal-fired boilers, Rynek Energii 105 (2) (2013) 61–64.

[3] N. Frank, Introduction and historical review of electron beam processing for environmental pollution control, Radiat. Phys. Chem. 45 (6) (1995) 989–1002.

[4] J. Licki, Analytical methods and monitoring system for e-beam flue gas treatment process, Radiat. Phys. Chem. 52 (1-6) (1998) 351–354.

[5] H. Namba, Pilot-scale test for electron beam purification of flue gas from coal-combustion boiler, Radiat. Phys. Chem. 46 (4-6) (1995) 1103–1106.

[6] A. Chmielewski, Operational experience of the industrial plant for electron beam flue gas treatment, Radiat. Phys. Chem. 71 (1-2) (2004) 439–442.
[7] A. Chmielewski, Optimization of energy consumption for nox removal in multistage gas irradiation process, Radiat. Phys. Chem. 45 (6) (1995) 1077–1079.