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ANDRZEJ G. CHMIELEWSKI*, JANUSZ LICKI**

APPLICATION OF ELECTRON BEAM FROM ACCELERATOR TO PURIFICATION OF EXHAUST GASES FROM COMBUSTION OF HIGH-SULPHUR FOSSIL FUELS

The irradiation of the exhaust gases from the burning of heavy fuel oil, mazout C-3, and the flue gases with high SO_2 content was carried out in INCT laboratory plant and in the pilot plant at TPP Kawęczyn, respectively. This procedure allowed these gases to be purified. The parametric study was conducted to determine the removal efficiency as the function of temperature and humidity of irradiated gases, absorbed irradiation dose and ammonia stoichiometry. The SO_2 removal efficiency above 95% and NO_x removal above 75% were obtained when the values of the process parameters were properly adjusted. The synergistic effect of high SO_2 concentration and irradiation on NO_x removal was observed. The collected by-product was the mixture of ammonium sulphate and nitrate with very low concentration of heavy metals.

1. INTRODUCTION

Most of the worldwide heat and energy (88% [1]) is produced by the combustion of such fossil fuels as oil, natural gas and coal. Carbon, hydrogen and oxygen are essential constituents of all these fuels which also comprise other components, including sulphur, nitrogen compounds and metals. Unfortunately, the combustion of fossil fuels is responsible for the emission of many pollutants that impact our air quality, human health, environment and economy as well as contributes to climate changes. Most of the world's fuels contain excessive amounts of sulphur, which is converted into sulphur dioxide when fuel is burnt. Additionally, the combustion process creates various forms of nitrogen oxides. The fuel with sulphur content up to 1.0% by weight is called a low-sulphur fuel and the fuel with sulphur content higher than 1.5% wt. is called a high-sulphur fuel. Sulphur content in Polish hard coal ranges from 0.8 to 3.8% wt. There are vast resources of high-sulphur coal in Spain, England, South Africa, Ukraine and the eastern States of America. The substantial resources of

* Institute of Nuclear Chemistry and Technology (INCT), ul. Dorodna 16, 03-195 Warsaw, Poland.
** Institute of Atomic Energy, 05-400 Otwock-Świerk, Poland.

lignite with the sulphur content higher than 2.5% wt. are found in the Maritza-East Region (Bulgaria) where big thermal power plants (TPPs) are installed. Heavy fuel oils (HFO) are the mixture of hydrocarbons composed of residual fractions from distillation and processing of crude oil. HFO is essentially an industrial fuel being suitable for use in thermal power plants, refineries, industrial boilers, pulp and paper industry, marine applications and metallurgical operations, which generally preheat the fuel oils. Depending on the source, the sulphur content in the HFO could be as high as 4% wt. Flue gas emitted as a result of combustion of high-sulphur fuel contains high SO_2 and NO_x concentrations, many times exceeding the permissible emission limits, which necessitates the use of add-on control device for the reduction of SO_2 and NO_x emissions. The study of the application of electron beam flue gas treatment (EBFGT) process to the purification of such flue gas was the task of this paper.

2. STATUS OF ELECTRON BEAM FLUE GAS TREATMENT TECHNOLOGY

The EBFGT technology is among the promising advanced technologies of new the generation. It is a dry-scrubbing process of simultaneous SO_2 and NO_x removal, where no waste is generated. In this technology, the temperature and humidity of flue gas are modified in the spray cooler, then almost stoichiometric amount of ammonia is added to the flue gas and such a gas mixture is irradiated in the process vessel by the electron beam from accelerator. The by-product is collected by the electrostatic precipitator (ESP) and may be used as an agricultural fertilizer or as a component of NPK or NPKS commercial fertilizer. This technology was implemented in a full-industrial scale at the Electric Power Station (EPS) "Pomorzany" in Szczecin for purification of flue gases emitted from two low-sulphur coal-fired Benson boilers. In this industrial plant with a nominal flow rate of 270 000 m_n^3/h, SO_2 and NO_x are removed from flue gas with the efficiency exceeding 90% and 70%, respectively [2].

3. RADIATION TREATMENT OF EXHAUST GASES EMITTED DURING COMBUSTION OF HIGH-SULPHUR FUELS

The applicability of EBFGT technology to purification of flue gas produced during combustion of high-sulphur fuels was tested at two plants.

3.1. PILOT PLANT AT THERMAL POWER PLANT "KAWĘCZYN"

The pilot plant built at TPP "Kawęczyn" is designed for electron beam irradiation of flue gases emitted from coal-fired boiler WP-120 (figure 1) [3].

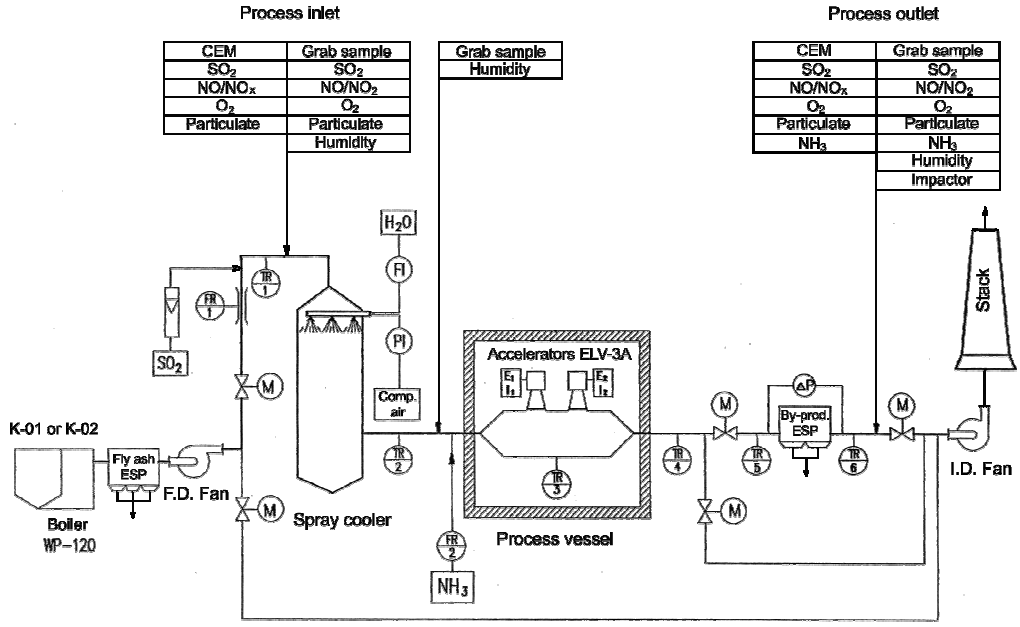

Fig. 1. Schematic flow diagram of pilot plant at TPP "Kawęczyn"

The hard coal with the sulphur content of about 0.7% wt. was burnt in a boiler and SO_2 concentration in the flue gas approximated to 500 ppmv. At the pilot plant inlet, the gaseous SO_2 from cylinder was added in a sufficient quantity to the flue gas to increase its SO_2 concentration up to 3200 ppmv. The flue gas with high SO_2 concentration simulates an exhaust gas emitted during combustion of high-sulphur coal. The study was carried out at the flow rate of 10 000 m_n^3/h of flue gas irradiated in the process vessel (PV) by the electron beam emitted from two ELV-3A accelerators (two-stage irradiation).

3.2. LABORATORY PLANT AT INSTITUTE OF NUCLEAR CHEMISTRY AND TECHNOLOGY (INCT)

The laboratory plant built at INCT [3] was adapted to the burning of heavy fuel oil mazout C-3 with sulphur content of about 3 % wt. (figure 2).

The natural flue gas was irradiated in the process vessel by the electron beam emitted from ILU-6M accelerator (one-stage irradiation).

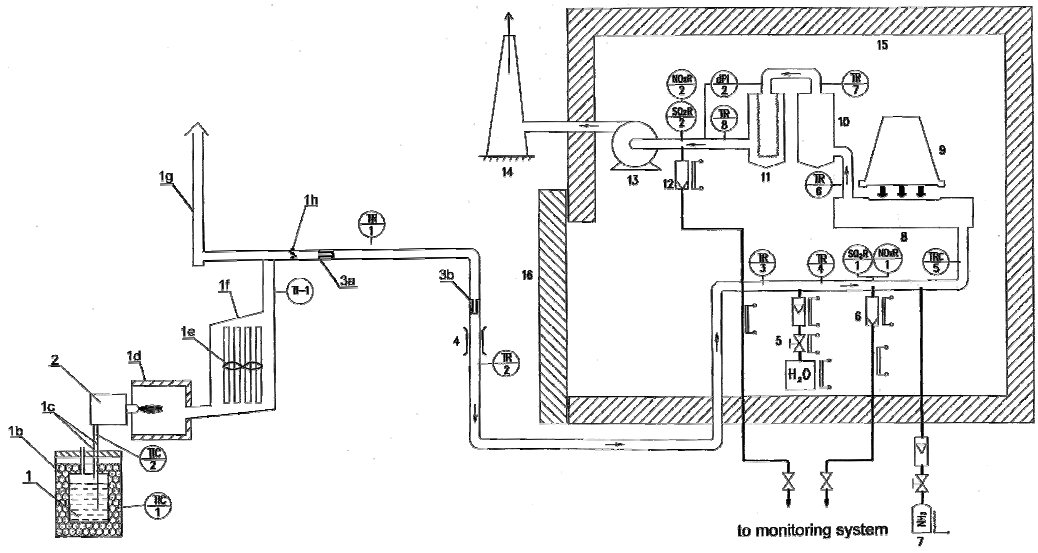

Fig. 2. Schematic diagram of laboratory plant at INCT for the treatment of flue gas from burning of high-sulphur heavy fuel oil:

1 – thermostated fuel oil,
2 – oil burner,
3 – particulate and soot 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

3.3. ANALYTICAL SYSTEM

The reliable and precise measurements of flue gas parameters in the crucial points of the plant are necessary for its proper operation and control. Figure 1 schematically depicts the places where these measurements were carried out. Two independent extraction multi-gas systems were installed to monitor the relevant constituents of the flue gas; one at the process inlet labelled with System-1 (upstream of the spray cooler) and the other at the process outlet labelled with System-2 (downstream of the ESP or bag filter). Each system consists of:

– SO_2 analyzer, Model 40, pulsed fluorescent.

– NO/NO_x analyzer, Model 10A/R, chemiluminescent.

– Model 900 for heated sample gas conditioning and dilution. Dilution ratio 20:1.

At the process outlet (System-2), the concentration of unreacted ammonia was determined by chemiluminescent analyzer, Model 17C, with two converters. All these

gas analyzers were manufactured by Thermo Environmental Instrument Co. (TEI from USA). Analyzer 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 sulfate, nitrate and ammonium ions along with water and insoluble content.

4. RESULT AND DISCUSSION

In the previous studies of this technology, it was demonstrated that the efficiencies of SO_2 and NO_x removal depend on the following process parameters: an absorbed dose (D) of irradiation, ammonia stoichiometry α_{NH_3}, gas temperature at the inlet to the 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 were performed at both plants.

4.1. EFFECT OF ABSORBED DOSE

Figure 3 presents the dependence of the irradiation dose on SO_2 and NO_x removal efficiency.

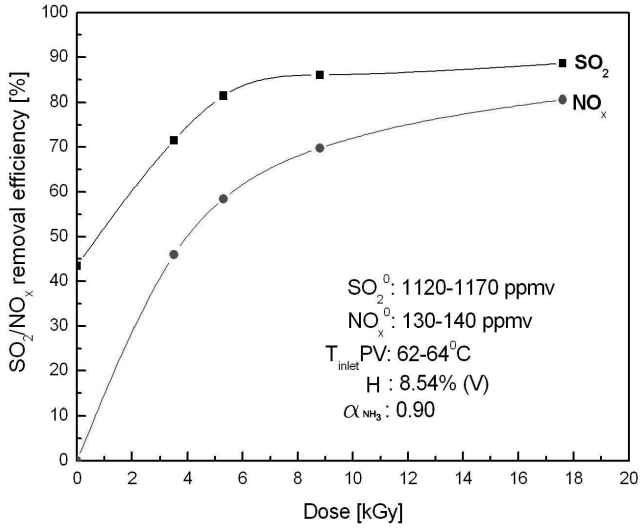

Fig. 3. Effect of absorbed dose on efficiencies of SO_2 and NO_x removal from flue gas obtained from burning of heavy-fuel oil, mazout C-3

The absorbed dose is the primary factor influencing NO_x removal efficiency. The process starts at zero efficiency for zero dose and indicates saturation at high doses.

This proves that NO_x removal is a radiation-induced process. A higher absorbed dose induces higher NO_x removal. The SO_2 removal is based on two different pathways: thermal process and radiation-induced process. At zero dose, SO_2 removal is governed by thermal reaction of SO_2 and NH_3 in moist environment. This reaction takes place in the gaseous phase as well as on the surfaces such as those on the filter cake of bag filter. Sulphur dioxide removal increases sharply with an increase of irradiation dose up to 8 kGy and then flattens out at high doses.

4.2. EFFECT OF AMMONIA STOICHIOMETRY

The efficiency SO_2 removal increases markedly with the increase of ammonia concentration in the irradiated flue gas. Above $\alpha_{NH_3} = 0.9$ this increase is gradual. The efficiency of NO_x removal slightly increases with ammonia addition. Fractions of the ammonia added remain unreactive and exist in the plant outlet (the so-called ammonia slip). In practice, it is desirable to keep the ammonia slip concentration as low as possible due to its harmful effect on environment. In the experiments performed at the pilot plant at TPP "Kawęczyn", the optimum ammonia stoichiometry should be about 0.9. In this case, the optimum efficiency of removal is obtained for both pollutants, as well as for slight ammonia slip (lower than 10 ppmv).

4.3. EFFECT OF GAS TEMPERATURE AT INLET TO PROCESS VESSEL

Figure 4 presents the effect of gas temperature on the efficiency of SO_2 and NO_x removal.

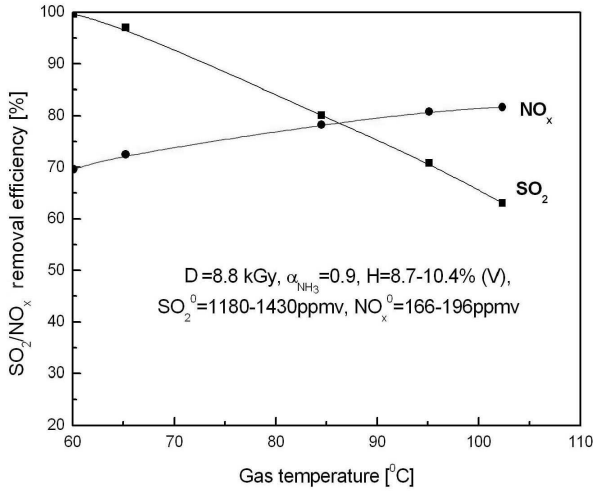

Fig. 4. Effect of gas temperature on efficiencies of NO_x and SO_2 removal

The efficiency of SO_2 removal significantly increases with the drop in gas temperature. This is in contrast with NO_x removal, which increases with the increase of gas temperature. Gas temperature has a significant impact on the SO_2 removal and small effect on the efficiency NO_x removal. 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 of 60–70 ºC to obtain high efficiency of SO_2 removal.

4.4. EFFECT OF FLUE GAS HUMIDITY

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

4.5. EFFECT OF INLET HIGH SO_2 CONCENTRATION

Figure 5 presents the effect of high inlet SO_2 concentration on the efficiency of NO_x removal.

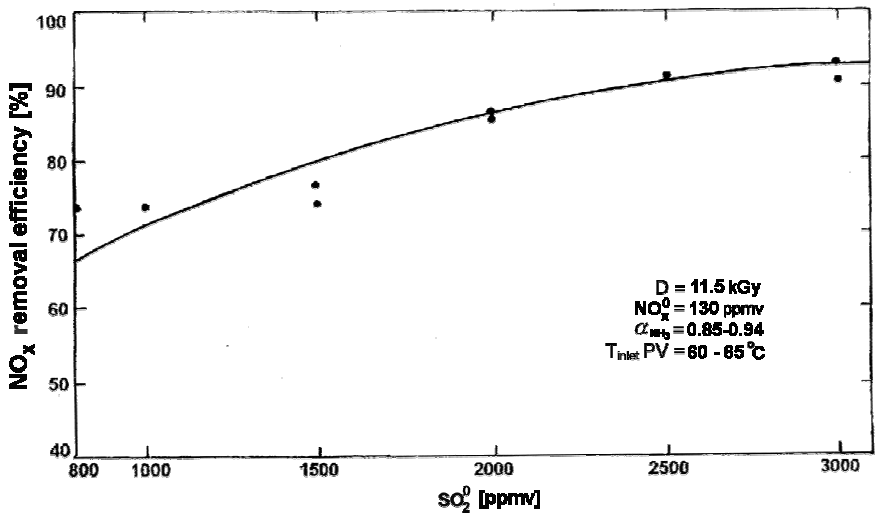

Fig. 5. Effect of inlet high SO_2 concentration on efficiency of NO_x removal

At a given dose (11.5 kGy in figure 5) a definite improvement of NO_x removal with an increase of high SO_2 concentration was observed. This synergistic effect of high SO_2 concentration is explained by the following radiation-induced reaction cycle [4]:

$$SO_2 + {}^{\bullet}OH + M \rightarrow HSO_3 + M,$$

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2^{\bullet},$$

$$NO + HO_2^{\bullet} \rightarrow NO_2 + {}^{\bullet}OH,$$

$$NO_2 + {}^{\bullet}OH + M \rightarrow HNO_3 + M.$$

In the second reaction, the $HO_2^{\bullet}$ radicals are formed, which efficiently oxidize NO and regenerate the previously depleted ${}^{\bullet}OH$ radicals. 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.

5. CONCLUSIONS

Flue gases from combustion of high-sulphur fossil fuels can be effectively purified by their irradiation with an electron beam. The removal efficiencies of SO_2 and NO_x exceeding 95% and 75%, respectively, were obtained under the optimum treatment conditions. These efficiencies can be obtained, first of all, by a proper controlling of 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 entering the inlet of a process vessel. Next, the mixture should be irradiated with an adequate irradiation dose in a process vessel. The improvement in NO_x removal is achieved by multi-stage irradiation and by an adequate dose distribution between irradiation stages [5]. The gas humidity and temperature, ammonia stoichiometry and irradiation dose up to 8 kGy strongly influence the efficiency of SO_2 removal. The synergistic effect of high SO_2 concentration and irradiation 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 that acceptable for commercial fertilizer.

ACKNOWLEDGEMENTS

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ZASTOSOWANIE WIĄZKI ELEKTRONÓW Z AKCELERATORA DO OCZYSZCZANIA SPALIN ZE SPALANIA ZASIARCZONYCH PALIW KOPALNYCH

Badano proces napromieniowania zasiarczonych spalin wiązką elektronów z akceleratora. Badania przeprowadzono na instalacji laboratoryjnej IChTJ (napromieniowywano gazy odlotowe ze spalania zasiarczonego oleju opałowego, mazutu C-3) i na pilotowej instalacji w EC Kawęczyn (napromieniowywano spaliny węglowe z dużą zawartością SO_2). Określono wpływ temperatury i wilgotności napromieniowywanych spalin, dawki zaabsorbowanej i stechiometrii dozowanego do spalin amoniaku na usunięcia SO_2 i NO_x. W optymalnych warunkach napromieniowania zasiarczonych spalin SO_2 był usuwany w 95%, a stopień usunięcia NO_x przekroczył 75%. Zaobserwowano synergetyczny wpływ dużego stężenia SO_2 i napromieniowywania na usunięcie NO_x. Wytworzony w procesie produkt końcowy jest mieszaniną siarczanu i azotanu amonu ze znikomą zawartością metali ciężkich.