



A dual-use of DBD plasma for simultaneous NO_x and SO₂ removal from coal-combustion flue gas

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ABSTRACT

Dielectric barrier discharge (DBD) was investigated for the simultaneous removal of NO_x and SO₂ from flue gas in a coal-combustion power plant. The DBD equipment was used in either a mode where flue gas was directed through the discharge zone (direct oxidation), or a mode where produced ozonized air was injected in the flue gas stream (indirect oxidation). Removal efficiencies of SO₂ and NO for both methods were measured and compared. Oxidation of NO is more efficient in the indirect oxidation, while oxidation of SO₂ is more efficient in the direct oxidation. Addition of NH₃, has lead to efficient removal of SO₂, due to thermal reaction, and has also enhanced NO removal due to heterogeneous reactions on the surface of ammonium salt aerosols. In the direct oxidation, concentration of CO increased significantly, while it maintained its level in the indirect oxidation.

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1. Introduction

In recent years, coal use has risen by 2.2% per year, faster than any other fuel. The use of coal is expected to rise by over 70% from 2005 to 2030, with developing countries responsible for 97% of this increase. Coal's share in global electricity generation is set to increase from 40% to 45% by 2030 [1]. In Serbia over 60% of electrical energy is produced by coal-burning power plants.

With the rapid increase in electrical power industry, coal-combustion electrical power plants will emit ever larger amounts of sulfur dioxide (SO₂) and nitrogen oxides (NO_x). The SO₂ and NO_x gases are the main cause of acid rain and urban air pollution. For large-scale emitters, devices for flue gas desulfurization implement control of SO₂ concentration by trapping it as calcium-sulfate (CaSO₄) in a lime–limestone mixture, while the removal of NO_x gases is performed by a separate process, selective catalytic reduction (SCR). While these processes have shown high removal efficiencies, high capital and operating costs and the added trouble of waste disposal are acknowledged as significant problems. SO₂ and NO_x coexist in coal flue gas but at this moment there are no reliable chemical methods for simultaneous removal of both SO₂ and NO_x in a single-stage process. Therefore, development of technology for simultaneous removal of SO₂ and NO_x (deSO₂/deNO_x)

is needed in order to reduce the operation costs. One promising candidate for such technology is the use of nonthermal plasma. The removal strategy of NO_x and SO₂, using nonthermal plasma, is based on oxidation of NO_x and SO₂ to their acid products, followed by neutralization through addition of ammonia to produce solid ammonium sulfate and ammonium nitrate. The mixture of mentioned ammonia products, with a small portion of collected fly ash, is acceptable as an agricultural fertilizer [2].

Nonthermal plasmas for deSO₂/deNO_x are usually created in essentially two different ways: electron-beam irradiation and electrical corona discharge [3]. Since the e-beam devices are capital intensive, many groups studied the treatment of flue gas using corona discharges. The pulsed corona discharge showed encouraging results for the simultaneous removal of NO_x and SO₂ [4], but energy efficiency obtained for the deNO_x/deSO_x reaction by e-beam irradiation is still better by a factor of two than for pulsed streamer corona [5]. DeSO₂/deNO_x from flue gas using pulse corona discharge was demonstrated at industrial level experiments with flow rates from 1000 N m³/h to 50,000 N m³/h [6–9]. A pilot plant for deSO₂/deNO_x from coal boiler flue gases was realized using a DC corona discharge ammonia radical injection technique [10]. Another nonthermal plasma technique which is used for deSO₂/deNO_x from combustion flue gases is the application of the dielectric barrier discharge (DBD) [11]. This type of discharge is widely used for ozone synthesis in industry [12]. Plasma characteristics and its energy efficiency in processes of removing NO are similar as in pulsed corona discharge [13]. Nonthermal plasma sources (DBD and corona discharge) are also used for production of ozone which is then used for low-temperature oxidation processes

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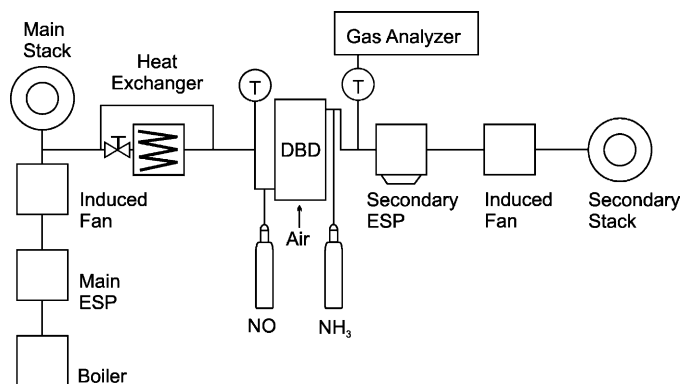


Fig. 1. Scheme of experimental facility. T – gas temperature measurement.

in simultaneous $\text{deSO}_2/\text{deNO}_x$ operation [14,15]. In this method ozone is produced in a free-standing reactor located outside of the polluted gas transporting duct and injected into a reaction chamber.

All the mentioned experiments and accumulated experiences were the starting point for our research of possible application of DBD plasma for treatment of flue gas from coal-combustion power station Nikola Tesla A (TENT A) in Obrenovac in Serbia. We have decided to use DBD in flue gas treatment, because its power supply is simpler and more reliable than the pulsed corona power supply. Distances between electrodes in DBD are several millimeters, which are at least one order smaller than in corona discharge, while concentrations of short-lived radicals (O^\bullet , OH^\bullet , HO_2^\bullet) are much higher. In real flue gas treatment small inter-electrode distance could present a serious problem due to flow obstruction. Specifically, the residual flying ash, which was not collected by electrostatic precipitator (ESP), becomes charged in the DBD, sticks on its electrodes and obstructs the gas flow. Absolute water vapor fraction in the real flue gas is up to 20%, therefore we expected that water condensate inside the DBD would remove the ash attached to the electrode surface, similarly to the process in the wet-type plasma reactors, see Refs. [16,17]. Since DBDs are frequently used as ozone generators, it was our intention to compare the treatment of flue gas using direct and indirect oxidation methods. In the direct oxidation method flue gas flows through the DBD whereas in the indirect oxidation method ozonized air, generated in the same DBD, is injected into the flue gas. Similar comparison was performed in an earlier laboratory experiment but with use of simulated flue gas [18].

2. Experiment

The experimental facility was built near a power plant unit of 200 MW and located after the main ESP. This experimental facility was projected for gas flow of up to $200 \text{ m}^3/\text{h}$, which was bypassed from the flue gas stream with flow of $1,200,000 \text{ m}^3/\text{h}$. The layout of the facility is shown in Fig. 1. It consists of a heat exchanger (not used in this experiment), DBD reactor, the secondary ESP for collection of ammonium salts produced by the process, and a fan for flue gas flow control. Gas temperatures were measured before and 1.5 m after the DBD reactor while gas analyses were performed 1.5 m after the DBD reactor, at entrance of the secondary ESP. Gas analyses were carried out using a gas analyzer (MRU VarioPlus Industrial) with electrochemical sensors for NO, NO_2 , SO_2 , O_2 and CO and an NDIR sensor for CO_2 . During our experiment, the coal boiler operated at low power resulting in low concentrations of NO and SO_2 in flue gas. In this experiment, additional NO gas was injected into the flue gas upstream from the DBD reactor to simulate the largest NO concentration, which could be reached only at maximum boiler operation power. After mixing with ambient

air, we were able to change concentration of NO from 50 ppm to 300 ppm while concentration of SO_2 was up to 300 ppm. Schematic diagram of the experimental setup for comparison of direct and indirect oxidation method is presented in Fig. 2. In both methods NH_3 was injected downstream from the DBD reactor. Ammonia presence at the measurement point was detected using Nessler's reagent with detection limit of 3 ppm. It should be noted that electrochemical sensors for NO_2 and SO_2 may be damaged in reactions with NH_3 . Because of that, special precaution was made in experiments with NH_3 : the intake of ammonia was set at such level so that its concentration at the specific measurement point was below the detection limit of Nessler's reagent. DBD reactor presented in Fig. 2c consists of 14 discharge tubes connected in parallel in one water cooled/heated stainless steel body. The outer and inner electrodes are made from stainless steel tubes, 1400 mm long, 40 and 21 mm in diameter, respectively. Glass barrier tubes (diameter – 32 mm, thickness – 1.5 mm, length – 1500 mm) are placed coaxially. The gap between the barrier and each electrode was set to 4 mm. The power supply consists of a 220 V–20 kV transformer which was excited by the line voltage at 50 Hz.

The ESP for collecting the by-product aerosol particles was placed 3 m downstream from the DBD reactor. The ESP has wire-to-plate design with volume of 0.7 m^3 and consists of nine plates with dimensions of $700 \text{ mm} \times 1500 \text{ mm}$. Distance between the plates is 76 mm; wire-plate distance is 38 mm; wire-to-wire distance is 100 mm; wire diameter is 0.8 mm and the total wire length is 67 m. The ESP operates at 18 kV DC.

The working flue gas was obtained by extracting the fraction from the main flue gas flow. The conditions of the working flue gas were: temperature $\sim 100^\circ\text{C}$ and absolute water vapor fraction of 12%.

In the direct oxidation method this gas was introduced into the DBD reactor, see Fig. 2a. In order to avoid water condensation inside the reactor, the entire reactor was heated to the temperature of about 95°C . Air flow through the reactor in the direct oxidation method, as shown in Fig. 2b, is needed only to obtain similar gas mixture as in the indirect oxidation method. Temperature of the analyzed gas mixture was $\sim 80^\circ\text{C}$. Throughout the experiment gas flow rate was kept at $150 \text{ m}^3/\text{h}$, which was the maximal flow rate for correct functioning of the DBD.

In the indirect oxidation method, working flue gas was mixed with ozonized ambient air at the exit of the DBD reactor, see Fig. 2b. In this method the DBD was used as an ozonizer which required water cooling. Temperature of analyzed gas mixture was about 75°C and absolute humidity was 15%.

In both methods the air flow was $\sim 15\%$ of the flue gas flow. The flow rates of flue gas were the same in direct and indirect oxidation methods. Also, the flow rates of the ambient air were the same for both oxidation methods.

To investigate the NO oxidation dependence on the composition of flue gas we performed measurements with two different gas mixtures, which were obtained using two different air flow rates through the DBD. The operating gas compositions used in this experiment were: 16% O_2 , 5% CO_2 , 12% H_2O , and 17% O_2 , 4% CO_2 , 12% H_2O . With both gas compositions the rest gas was N_2 , with more than $100 \text{ mg}/\text{m}^3$ of fly ash.

3. Results and discussion

3.1. DeNO_x

Concentrations of NO and NO_2 were measured in both the direct and the indirect oxidation method for flue gas treatment. Dependences of concentration of these gases on input energy density (in Joules of plug-in energy per standard liter) are given in Fig. 3. Limi-

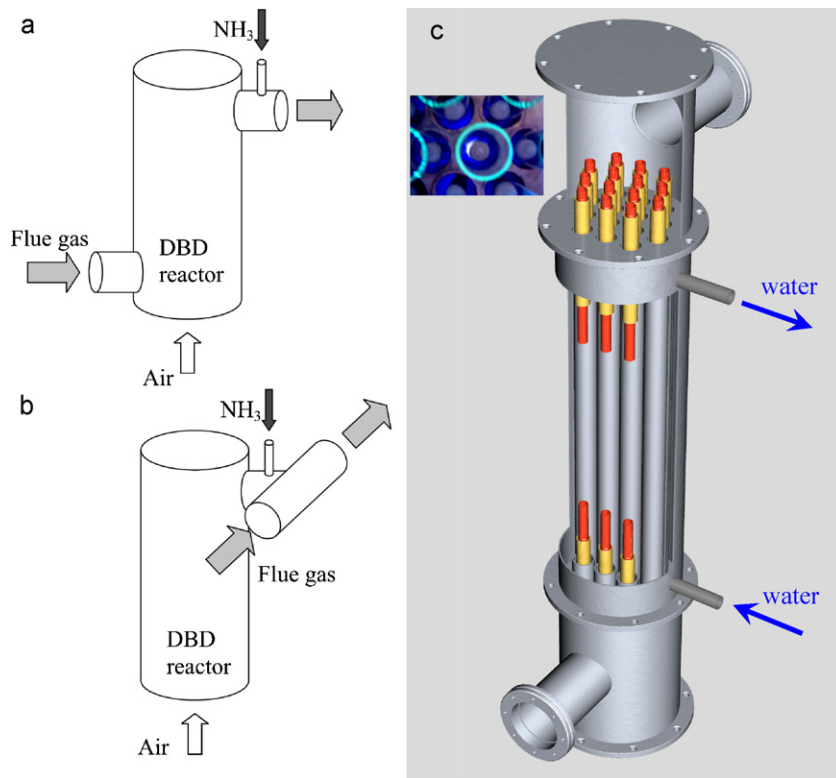
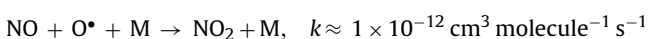
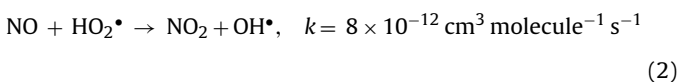
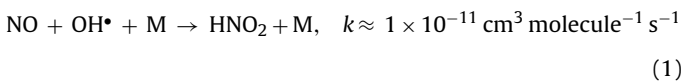


Fig. 2. Schematic picture of (a) direct oxidation method, (b) indirect oxidation method and (c) scheme of the DBD reactor with photograph of longitudinal view of its electrode system during the test operation in air.

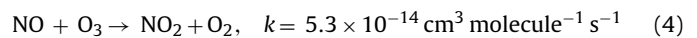
tation of our power supply determined the maximal value of input energy, and consequently maximal possible removal of NO. The figures also show concentration of NO_x which is the sum of NO and NO₂ concentration. Concentrations of nitric oxides were recorded with two different compositions of flue gas mixture with ambient air. Hollow symbols signify air–flue gas mixture with 16% O₂ and 5% CO₂, and solid symbols signify gas mixture with 17% O₂ and 4% CO₂. Differences between the graphs of two gas compositions are negligible. Fortunately, gas composition in our experiment, had high concentration of O₂ and H₂O (16% O₂ and 12% of H₂O), which enabled the forming of a more extensive and reactive set of radicals (O•, OH• and HO₂•) for the oxidation of NO. These radicals are necessary for efficient removal of NO in a non-thermal plasma [19,20].

The process of NO_x removal can be divided into two stages: NO oxidation to NO₂ and NO₂ conversion to ammonium-nitrate [20].

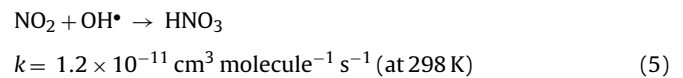
In the direct oxidation method, NO is oxidized by OH, HO₂ and O radicals and by O₃ which are produced in the inter-electrode space. Oxidation reactions are very fast [21]. Rate coefficients for reactions are calculated at a temperature of 360 K according to equations presented in Ref. [21]. In three body reactions, rate coefficients are calculated using estimated concentration for M ([M] = 2 × 10¹⁹ molecule cm⁻³ at atmospheric pressure and 360 K).



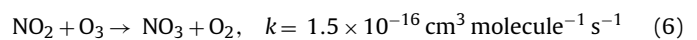
(3)



The second stage of the DeNO_x process is NO₂ removal. In the discharge region of the DBD, the NO₂ is oxidized mainly by OH radicals to form HNO₃.

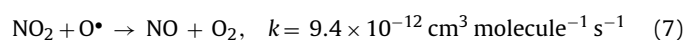


NO₂ can also be oxidized to NO₃ by O₃ which is of interest in indirect oxidation method.



Due to low chemical activity of ozone with respect to NO₂, the oxidation by ozone is not an important process in the direct oxidation method. However, it becomes more important in the indirect oxidation method since highly reactive radicals, O•, OH• and HO₂•, are not present in the reaction zone.

Fig. 3 shows that concentration of NO decreases with increasing input energy density for both methods. This is because the production of radicals O•, OH•, HO₂•, and O₃ responsible for oxidation and removal of NO is proportional to the energy density. Comparing the figures, one can conclude that NO removal efficiency is higher for indirect oxidation method. Namely, in the direct oxidation method, oxidation of NO through the processes (1)–(4) is not a simple straightforward reaction sequence. Part of the intermediate NO₂ is reduced back to NO by oxygen atoms:



This back-reaction determines the energy density dependence of NO removal [20]. In the direct oxidation, NO_x (=NO + NO₂) concentration decreases because NO is oxidized to HNO₂, and NO₂ is oxidized to HNO₃, what in total decreases NO_x concentration, see

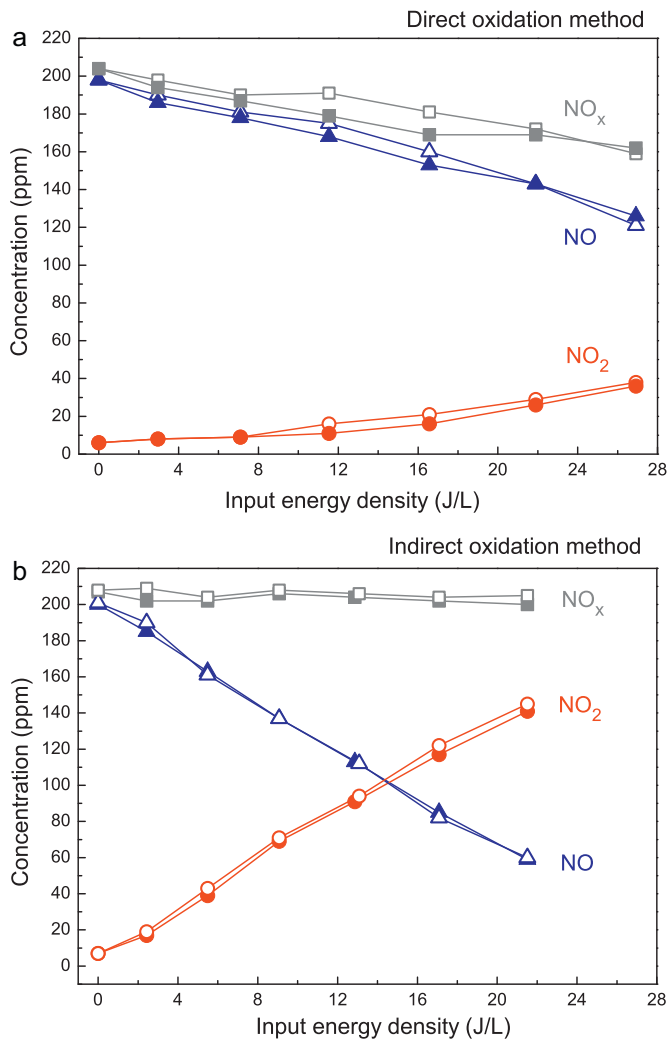


Fig. 3. Dependence of concentrations of nitric oxides versus density of energy deposited into the gas using (a) direct oxidation method and (b) indirect oxidation method. Initial concentrations (NO ~ 200 ppm; SO₂ ~ 250 ppm); gas temperature at measurement point (direct: 75 °C; indirect: 90 °C).

Fig. 4a. In a humid gas the concentration of hydroxyl radicals is large, and NO₂ reacts mainly with OH•, as was shown using simulation in another type of DBD [22], but conclusion is also applicable to our experiment.

In the indirect oxidation method flue gas was mixed with ozonized air in a mixing chamber placed 40 cm downstream from the DBD. At this point concentrations of O•, OH• and HO₂• radicals were negligible due to their very short lifetimes, so the main process for NO oxidation in this region is reaction with O₃ [22]. Due to the absence of the O• radical there is no back-reaction, so NO is more efficiently oxidized. As can be seen in Fig. 3b, concentration of NO_x remains constant. This is due to the fact that NO is oxidized to NO₂ by ozone, 300 times more efficiently, than NO₂ to NO₃, making the sum of NO and NO₂ nearly constant.

From the slow depletion of NO₂ we can conclude that its concentration will not decrease until no further formation from NO is possible i.e. NO reaches its minimum value. Precisely this effect is observed and presented in Fig. 4b, when initial concentration of NO has a lower value than 80 ppm. After the concentration of NO reaches its minimal value, concentration of NO₂ starts to decrease, as a consequence of oxidation to NO₃, by ozone. Decrease of SO₂ concentration is not so straightforward, because the rate for SO₂ oxidation by ozone is five orders lower than rate for NO₂ oxidation.

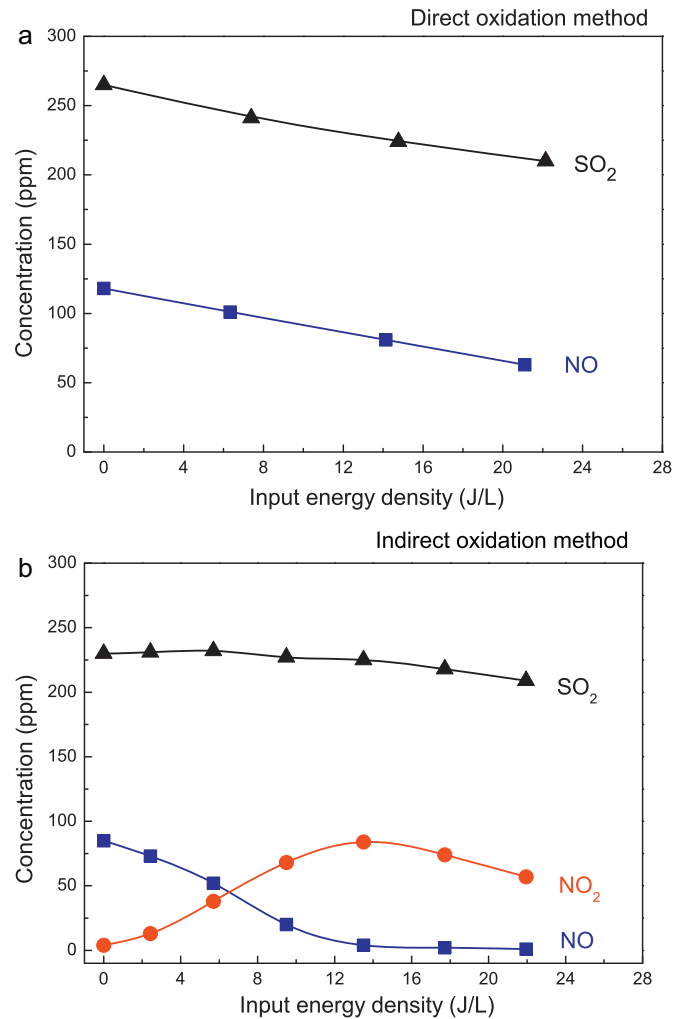
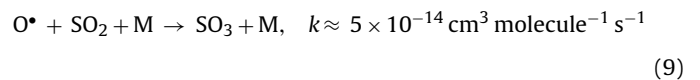
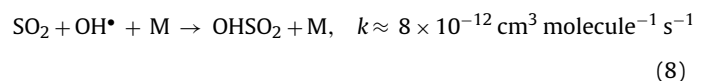


Fig. 4. DeSO₂ and deNO_x using (a) direct oxidation method and (b) indirect oxidation method. Initial concentrations (direct: NO ~ 120 ppm and SO₂ ~ 270 ppm; indirect: NO ~ 90 ppm and SO₂ ~ 230 ppm); gas temperature at measurement point (direct: 75 °C; indirect: 90 °C).

3.2. DeSO_x

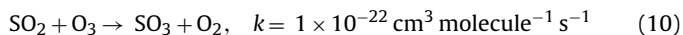
The removal of SO₂ is based on chemical changing of SO₂ into species that are easily removed from the flue gas. The removal process involves oxidation of SO₂ by O• and OH• radicals finally forming H₂SO₄. There are two main channels for oxidation:



Final products of reactions (8) and (9) react with water and form H₂SO₄. By comparing the rate coefficients one may observe that the reaction with OH• radical is more relevant. Furthermore, kinetic analysis has shown that in air discharge plasmas only OH• radical provides oxidation of SO₂ [20].

Fig. 4a shows that in direct oxidation in the DBD reactor, concentration of SO₂ continuously decreases with increase of input energy. Concentration of NO decreases with the similar rate, what is expected if the back-reaction (7) of removing NO is included along with reactions (1)–(4).

In the indirect oxidation method, at 40 cm distance downstream from the discharge, which corresponds to ~ 0.5 s in time scale, the only chemically active specie that remains is ozone. SO_3 removal using ozone could be provided by reaction [23]:



In comparison with this reaction, NO_2 oxidation by O_3 is more than five orders of magnitude faster, see rate coefficient in reaction (6). Having this in mind, decreasing of SO_2 concentration, as presented in Fig. 4b, could not be explained with oxidation by ozone. Because the gas phase oxidation of SO_2 by O_3 can be neglected, the main path of SO_2 oxidation has to be a heterogeneous process on the surface of fly ash particles in flue gas. This kind of process for SO_2 removal was recently observed in atmospheric chemistry, in an experiment of oxidation of SO_2 by O_3 on mineral dust [24]. This process proceeds via two major steps. The first step is a reversible adsorption of SO_2 on the surface followed by a second, irreversible, and very fast reaction, in which adsorbed SO_2 is oxidized to sulfate by ozone. The formation of sulfate on the surface was increased due to the presence of water vapor. Although atmospheric conditions are not similar to conditions in flue gases, we believe that mentioned process could satisfactorily explain the removal of SO_2 . It should be noted that influence of fly ash on deNO_x or/and deSO_2 , in corona discharges, has been investigated in several articles [25–27]. It was observed that a synergistic effects of water vapor and fly ash addition strengthen the chemical adsorption ability of the fly ash surface, which resulted in a considerable improvement in the conversion of NO and SO_2 . Humidity of the real flue gas in our experiment was $\sim 15\%$ with fly ash concentration of $\sim 100 \text{ mg/m}^3$. These are almost optimal conditions for increase of deNO_x and deSO_2 efficiency in the direct oxidation treatment [27].

3.3. NH_3 addition

Removal of SO_2 solely by use of a discharge has not been very successful so far (10–30%) [4,9,28]. Significant SO_2 conversion is possible only by using extreme input energy [28]. With addition of NH_3 in the flue gas, SO_2 removal has considerably increased. In our experiment, ammonia is used in concentration estimated according to the stoichiometric equivalence: 2 mole of NH_3 per 1 mole of SO_2 (needed for $(\text{NH}_4)_2\text{SO}_4$) plus 1 mole of NH_3 per 1 mole of NO_x (for NH_4NO_3). Although the removal of SO_2 is enhanced in the discharge, see Fig. 5, it is governed mainly by the thermo-chemical reaction with ammonia. In a presence of excess water vapor and oxygen, mainly ammonium sulfate is formed. In studies on the formation of aerosols of ammonium sulfate in humid air, the salt formation is always considered to occur in a heterogeneous process. It has been established that formation of aerosols is enhanced by discharge, so the removal efficiency of SO_2 was over 98% [28]. The removal of SO_2 can also be affected by heterogeneous chemical reaction between SO_2 , NH_3 , and H_2O on the surface of fly ash and also on the surface of formed particles of ammonium sulfate and ammonium nitrate. Although decrease of SO_2 , without NH_3 , is more pronounced using the direct oxidation method, we could not observe the difference in SO_2 removal between the two methods, when NH_3 was used. In both methods removal efficiency of SO_2 is better than 98% (below the detection limit of the gas analyzer). Since there are no differences in SO_2 removal using NH_3 between the two methods, and since removal processes are governed mainly by the well known thermo-chemical reaction, we did not present trivial graphs representing SO_2 removal.

The removal efficiency of NO , for the direct and the indirect oxidation method, both with and without addition of NH_3 is presented in Fig. 5. Analyzing the figure, one can conclude that addition of NH_3 increases the NO removal efficiency for both oxidation methods. In both cases influence of NH_3 is larger for higher NO concentration

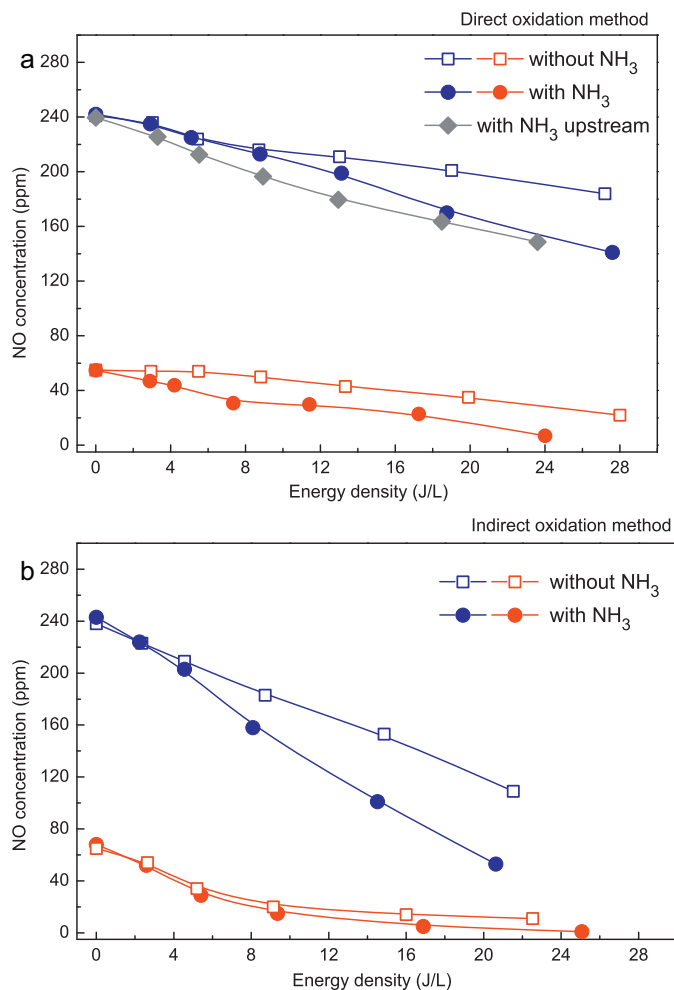


Fig. 5. Dependence of NO concentration on density of energy deposited into the gas using direct oxidation method (a) and indirect oxidation method (b) with addition of ammonia. Two different initial concentrations of NO are used (direct: $\text{NO} \sim 240$ ppm and $\text{NO} \sim 60$ ppm; $\text{SO}_2 \sim 270$ ppm; indirect: $\text{NO} \sim 240$ ppm and $\text{NO} \sim 70$ ppm; $\text{SO}_2 \sim 240$ ppm); gas temperature at measurement point (direct: 75°C ; indirect: 90°C).

and higher energy density. It has been observed in Ref. [28] that removal of NO is strongly enhanced by SO_2 or NH_3 . When all three gases were present in the experiment described in [28], this synergistic effect was observed only when NH_3 was introduced much further downstream than NO and SO_2 . This was done to prevent SO_2 and NH_3 from reacting too fast mutually, which would diminish the beneficial effect of NO removal. Following this conclusion, we wanted to observe the difference of NO removal for injection of NH_3 upstream and downstream from the DBD in direct oxidation method. The results are presented in Fig. 5a.

There are several reasons why NH_3 increases the efficiency of NO removal in the direct oxidation method. Firstly, when NH_3 is injected upstream from the DBD it reduces the effect of the back reaction $\text{NO}_2 \rightarrow \text{NO}$ caused by O^\bullet radical by transforming it to H^\bullet radical through reaction:



where NH_2 is produced from NH_3 in the discharge region. The H^\bullet radical is after that involved in NO oxidation through the channel $\text{H}^\bullet \rightarrow \text{HO}_2^\bullet \rightarrow \text{NO}_2$ [20]. The second reason for the enhancement of NO removal is the formation of NH_4NO_3 which removes NO_2 from the discharge and, consequently, disables the back-reaction. In this way, ammonium-nitrate improves not only NO_2 removal, but also

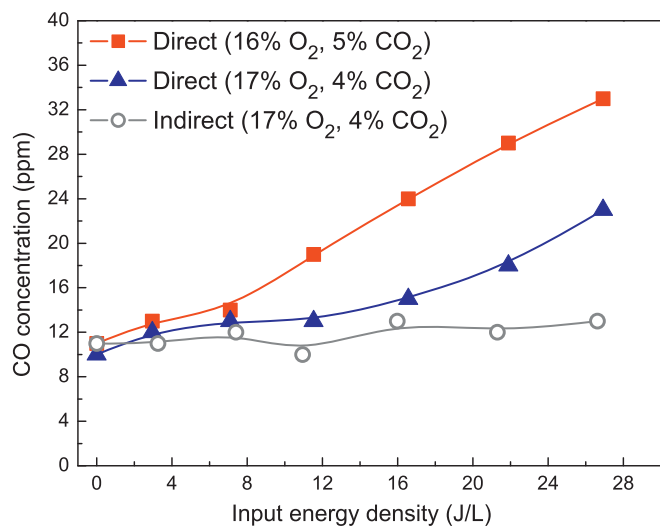


Fig. 6. Comparison of CO concentrations obtained using direct and indirect oxidation for different input energies and different gas mixtures. Gas temperature at measurement point (direct: 75 °C; indirect: 90 °C).

NO oxidation. SO₃ and NO₂, formed in the discharge, together with SO₂, react with NH₃ and, in the presence of water, form ammonium salt aerosols. In an experiment with pulsed-corona very high removal of NO_x was measured, when in situ ammonium salt aerosols were formed in a simulated flue gas that contained NH₃, SO₂, and ozone [29]. In the real flue gas, as in our experiment, fly ash particles are also present with a non negligible concentration. These particles, together with the ammonium salt aerosols, serve as highly efficient adsorbents with large surface area and enhance the heterogeneous chemical reactions of NO_x removal. Although the reaction pathway is unknown, it is our presumption that radicals (O[•], OH[•], HO₂[•]), O₃, NO, H₂O and NH₃ were adsorbed on the surface of the mentioned adsorbents, which resulted in the oxidation of NO and formation of NH₄NO₃.

Analyzing Fig. 5a one can conclude that efficiency of NO removal is higher for NH₃ injected upstream. This is caused by suppression of back reaction NO₂ → NO, and by doubling the resident time in comparison with NH₃ injected downstream.

Increasing of NO removal efficiency by injecting NH₃ in the indirect oxidation method, see Fig. 5b, can only be explained by heterogeneous reactions on the surface of the adsorbents.

After the SO₂ and NO_x are removed from the gas phase, the final products, ammonium salt aerosols, are collected in a form of powder by the secondary ESP. This powder was then subjected to chemical and SEM analysis. Due to space limitations these results could not be presented here, and will be published in a forthcoming article. It should be noted that concentrations of heavy metals in the powder were below the limit values for fertilizers.

3.4. CO emission

There is a serious problem of concentration increase of toxic CO with the use of direct oxidation method, noted in [30]. Taking this into account we have measured CO concentrations in the direct and indirect oxidation methods in order to compare them. Fig. 6 shows dependence of CO concentration on energy density for two used oxidation methods. This figure shows that in the direct oxidation method CO concentration rises with increase of energy transferred to the gas.

Numerical simulation for barrier discharge also predicts such behavior of CO concentration [22]. The main channel for production of CO is the decomposition of CO₂, caused by excited nitrogen

molecules N₂^{*}, whose concentration is very large in the barrier discharge. Having this in mind, it is clear that increase of CO₂ concentration will increase CO concentration, as is shown in Fig. 6. In the direct oxidation, CO concentration has increased more than double its original value, while it remained constant when the indirect oxidation method was used. In the indirect method there are no radicals which could participate in decomposition of CO₂ to CO, so the concentration of CO remains unchanged as shown in Fig. 6.

4. Conclusion

Two methods for use of DBD for simultaneous removal of NO_x and SO₂ from the real flue gas in a power plant have been presented. The first method, direct oxidation (flue gas flows through the discharge), and the second method, indirect oxidation (ozonized air is injected in flue gas), are compared by measuring removal efficiency of SO₂ and NO. It is concluded that oxidation of NO is more efficient in the indirect oxidation, while oxidation of SO₂ is more efficient in the direct oxidation. In the direct oxidation of NO, besides its oxidation to NO₂ there also exists a back reaction which transforms NO₂ to NO and effectively decreases NO removal. In the indirect oxidation of NO there are no back reactions. SO₂ oxidizes to SO₃ in the discharge mainly by OH[•] radical, while SO₂ oxidation by ozone is only possible as a heterogeneous reaction on the surface of fly ash particles. The injection of NH₃ very efficiently removed SO₂ from the flue gas due to the thermal reaction of SO₂ with NH₃ and formation of ammonium salts. NH₃ has also increased NO removal predominantly due to heterogeneous reactions on the surface of ammonium salt aerosols. It should be noted that in the direct oxidation, concentration of CO has increased more than twice, while it was unchanged when the indirect oxidation was used.

Acknowledgments

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