Medium-scale experiments on DeNo/DeSO\textsubscript{2} from flue gas by pulsed corona discharge
Zhou, L.M.; van Veldhuizen, E.M.

Published: 01/01/1996
Medium-scale Experiments on DeNO/DeSO2 from Flue Gas by Pulsed Corona Discharge

by
L.M. Zhou
E.M. van Veldhuizen

EUT Report 96-E-302
ISBN 90-6144-302-4
December 1996
Medium-scale Experiments on DeNO/DeSO2 from Flue Gas
by Pulsed Corona Discharge

by

L.M. Zhou
E.M. van Veldhuizen

EUT Report 96-E-302
ISBN 90-6144-302-4

Eindhoven
December 1996
Zhou, L.M.


NUGI 832

Trefw.: ontzwavelen / stikstofoxiden / coronas / elektrische gasontladingen / rookgassen / hoogspanningspulsen.

Subject headings: flue gas desulphurisation / corona / electric discharges / pulsed power technology.
Medium-scale experiments on DeNO/DeSO₂ from flue gas by pulsed corona discharge

Zhou L.M. and E.M. van Veldhuizen

Abstract
Pilot-scale experiments on the simultaneous removal of SO₂ and NOₓ from flue gases have been conducted. UV absorption to simultaneously detect NO (0-450 ppm), SO₂ (0-1000 ppm) and NH₃ (0-1000 ppm) is applied to the flue gas cleaning process using pulsed corona discharge. The measurement error is in all cases below 5% despite of spectral overlap. The good agreement on the removal effects with results from literature shows that this is a viable method. Flue gases produced using a methane burner are treated in a pulsed corona reactor with 6-80 Nm³/h flow. The initial concentrations of SO₂ and NO are about 300 ppm in flue gas. The pulses of voltage with about 100 ns rising time and 180 ns half-width are used to produce the pulsed streamer discharges. The results show that the energy cost of the removal of NO and NOₓ can be reduced through optimizing the energization and gas conditions including de bias, temperature, residence time, synergetic effect of NO, SO₂ and NH₃. The auto-thermal reaction of SO₂-NH₃ is dominant for SO₂ removal. The increase in input of discharge energy has only a small influence on the SO₂ removal, but the slip of NH₃ can be reduced to almost zero by increasing the power input. It is observed that the removal rate of SO₂ depends to a great extent on the time sequence of experiments. This strong history effect is beneficial for SO₂ removal with corona discharge and NH₃ injection. NH₃ injection enhances the NO removal but its slip is high. SO₂ presence in flue gas enhances NO removal also, in combination with NH₃, however, the enhancement becomes less than either of them. Through adjusting locations of SO₂ or NH₃ injection, synergetic effects on NO removal can be greatly enhanced. With an optimum residence time of about 15 s and the use of history and synergetic effects, more than 95% SO₂ and 85% NO are removed with 3 ppm leak NH₃, resulting in an energy cost of 13 eV/NO. With shorter pulses, further improvement of NO removal is still expected to be possible.

Keywords: flue gas, SO₂/NOₓ removal, pulsed corona discharge, UV absorption, synergetic effect

- Zhou L.M. and E.M. van Veldhuizen
  Medium-scale experiments on DeNOₓ/DeSO₂ from flue gas by pulsed corona discharge.
  Eindhoven: Faculty of Electrical Engineering, Eindhoven University of Technology, 1996.
  EUT Report 96-E-302
- Addresses of the authors:
  Zhou Li-Ming
  Division of High Voltage, School of Electrical Engineering, Xi’an Jiaotong University
  Xi’an 710049, P.R. China

  E.M. van Veldhuizen
  Division of Electrical Energy Systems
  Faculty of Electrical Engineering
  Eindhoven University of Technology
  PO Box 513, 5600 MB Eindhoven, The Netherlands
Preface

This report is a summery of the experimental work at Eindhoven University of technology from December 14, 1995 to September 1, 1996. During this period, I was on leave from the Xi'an Jiaotong University and worked at the Eindhoven University as a postdoctoral fellow under the guidance of Dr. E.M. van Veldhuizen. My stay in Eindhoven is financially supported by EUT as a part of EUT-XJTU exchange programme.

My first thanks are given to Dr. E.M. van Veldhuizen for his guidance at each step of this research work. I wish to thank Prof. W.R. Rutgers for stimulating discussions and invaluable suggestions. I like to give my true thanks to Loek Bade for the close co-operation and always help during the experiments. I also like to give my thanks to Ad Holten and Wilfred Hoeben for their particular help on the computer. I like to thank my wife, Li Lin, who joined me from USA and supported me to complete this investigation.

Final thanks are ascribed to the Eindhoven University of Technology for the provision of a research scholarship.

Zhou Li-Ming

August, 1996
CONTENTS

1. Introduction  
1.1 General  
1.2 Current status  
1.3 Present objectives

2. Description of experimental system  
2.1 Flue gas cleaning set-up  
2.2 Pulse power supply  
2.3 UV absorption set-up

3. UV absorption measurements  
3.1 Absorption spectra  
3.2 Calibrations

4. Cleaning measurements  
4.1 Removal of NO/NO\textsubscript{x}  
4.1.1 DC bias effect  
4.1.2 Residence time effect  
4.1.3 O\textsubscript{3} and H\textsubscript{2}O effect  
4.1.4 Temperature effect

4.2 Removal of SO\textsubscript{2}  
4.2.1 Removal of SO\textsubscript{2} in air  
4.2.2 Removal of SO\textsubscript{2} in flue gas  
4.2.3 History effect

4.3 Combined removal of NO and SO\textsubscript{2}  
4.3.1 SO\textsubscript{2} effect on DeNO/DeNO\textsubscript{x}  
4.3.2 Synergetic effect of SO\textsubscript{2}, NO and NH\textsubscript{3}  
4.3.3 NH\textsubscript{3} effect on the removal of SO\textsubscript{2} and NO  
4.3.4 Enhancement of synergetic effect

5. Two-stage cleaning measurements  
5.1 NO and NO\textsubscript{x} removal  
5.2 Combined removal of SO\textsubscript{2} and NO

6. Removal of NH\textsubscript{3}

7. Discussion

8. Conclusions

9. References
1. Introduction

1.1 General

NO\textsubscript{x} and SO\textsubscript{2} emissions are the main cause of the acid rain. A increasing public and official concern calls for powerful treatment. To meet this requirement, combined removal of NO\textsubscript{x} and SO\textsubscript{2} (generally referred to as combined DeNO\textsubscript{x}/DeSO\textsubscript{2} from the flue gas by pulsed corona discharge has been comprehensively investigated in the past decade. The possibility of an application of pulsed corona discharges to simultaneous removal of SO\textsubscript{2} and NO\textsubscript{x} from the flue gas of coal-fired power stations has been experimentally confirmed at ENEL \cite{1}. Based on ENEL experimental results and compared with other processes (Calcium-Gypsum + Ammonia Catalytic, E-Beam), the pulsed corona method has presented the most economical means for the next generation DeNO\textsubscript{x}/DeSO\textsubscript{2} \cite{2}. The general advantages of pulsed discharge technology for industrial application are suggested as: (1) it simultaneously removes NO\textsubscript{x} and SO\textsubscript{2} in a single dry process; (2) it could be retrofitted in existing electrostatic precipitation; (3) it requires a low ground surface; (4) its by-product is dry powder which could be easily collected by an electrostatic precipitator; (5) the by-product could be directly used as an agricultural fertiliser.

1.2 Current status

During the DeNO\textsubscript{x}/De/SO\textsubscript{2} process with pulsed corona discharge in combination with ammonia injection, the pulsed corona induced chemical reactions are generally divided as essential radical initiated reactions and spontaneous reactions. For the removal of SO\textsubscript{2} auto-thermal reactions of SO\textsubscript{2}/NH\textsubscript{3} are supposed to play the most important role. In contrast, the NO\textsubscript{x} molecules are mainly oxidized by radical reactions. Comparatively, the removal of NO\textsubscript{x} is energy cost and its chemistry is also much more complex. Take ENEL experimental results as a typical example, 99 % SO\textsubscript{2} can be easily removed with corona discharge and NH\textsubscript{3} and H\textsubscript{2}O injection \cite{3}. But, the corona discharges alone can only convert about 10 % SO\textsubscript{2} in most cases. NO\textsubscript{x} removal mainly depends on the energy input of discharges. For this reason, the removal rate (%) and energy costs per removed NO\textsubscript{x} molecule (eV/NO\textsubscript{x}) from flue gas in the literature are generally used to evaluate the cleaning efficiency. At ENEL, 50-60 % of 250-500 ppm NO\textsubscript{x} is removed at the energy input of 12-15 Wh/Nm\textsuperscript{3}, corresponding to a minimum energy cost of 50 eV/NO\textsubscript{x} \cite{1}. It is estimated to be 5-6 % of power plant output. Such an energy requirement is still too high for commercial application. However, one should bear in mind that experiments up to now have been performed with a rather limited set of conditions mainly in an empirical way and small scale. The whole process is not fully optimized yet and the chemistry of the process is only superficially understood. Before this technology is put into practical application, it is essential to scale up the treatment process for obtaining a better understanding of the SO\textsubscript{2}/NO\textsubscript{x} conversion mechanism and finding the best technical approaches. Under this circumstance, systematic experiments are conducted to reveal the importance of experimental conditions. In the first stage, the pilot-scale experiments have confirmed the importance of optimization of gas conditions and energization parameters for improving the energy efficiency: without any additive the energy cost of 20 eV/NO has been obtained using voltage pulses with about 20 ns and a 60-70 °C flue gas with a residence time of 15 s \cite{4}. Although only a part of the parameters has been optimized in these experiments, they have already indicated that, with optimizing conditions, the energy cost can be lowered to satisfy a energy requirement of 1-2 % (less than 20 eV/NO ) of the output of the power plant.

1.3 Present objectives

The general objective of the investigation is to lower the energy cost at required removal rates of NO\textsubscript{x} and SO\textsubscript{2} in real flue gas. Regarding the amount of NH\textsubscript{3} injection, both improvements of SO\textsubscript{2} and NO\textsubscript{x} removal rates and the reduction of NH\textsubscript{3} slip (<5 ppm, in The Netherlands) will be taken into
account in the investigations. The present work at EUT, in general, consists of two subjects:

(1) Detection of $\text{SO}_2$, NO and NH$_3$ by UV absorption

As the first and essential step, UV absorption is developed to detect on-line and simultaneously NO, SO$_2$ and NH$_3$ in the cleaning process in order to avoid the interference of NH$_3$ injection on the previously used gas analyzer. The part of the results on this subject has been reported in [5].

(2) Cleaning measurements on removal of SO$_2$ and NO$_x$

For the removal of NO/NO$_x$, the main attention will be paid to finding the optimum energization conditions including gas conditions and electrical parameters such as gas temperature, gas flow rate or residence time, dc bias level, NH$_3$ injection.

For the removal of SO$_2$, the auto-thermal reaction of SO$_2$-NH$_3$, corona discharge and both in combination are systematically investigated. The gas temperature and water content in the flue gas will be the main parameters in question.

For combined removal of SO$_2$ and NO with and without NH$_3$ injection, the synergetic effects between SO$_2$, NO and NH$_3$ will be mainly focused on. Positive effects are expected to lower the energy cost of the removal of NO$_x$.

Since some parameters, including pulse risetime and gas temperature, have been known the best values for the removal of NO at EUT [4], the present work is based on these previous investigations and to further optimize the cleaning process in flue gases with about 300 ppm NO and 300 ppm SO$_2$. The part of the results on this subject has also been presented in [6].
2. Description of experimental system

2.1 Flue gas cleaning set-up

An overview of the complete set-up at EUT is given in the figure 1. This pilot-scale system uses a methane burner with a maximum output of 300 Nm³/h [7]. The flue gas partly goes through a wire-cylinder corona reactor, which consists of two chambers in series with a length of 2.88 m and 2.77 m, respectively. The diameter of corona wire is 3 mm and the cylinder inner diameter is 0.2 m.

Figure 1: An overview of the complete pilot-scale set-up for flue gas cleaning at EUT
The reactor can be used to perform the single-stage (with 2.88 m chamber) and double-stage (with two chambers in series) flue gas treatment experiments. Although the parameters of electrodes such as the diameter of corona wire and the gap spacing are important for the optimisation, they are temporarily fixed in this work. The gas temperature in the reactor can be adjusted between 60 and 130 °C by the aid of the electrical heating and gas flow. The flue gas flow can be varied from 6 to 80 Nm³/h. The total gas flow through the corona section is measured with a pressure difference flange with 2 % accuracy. The typical flue gas from the burner has a composition of 6 % O₂, 8 % CO₂, 16 % H₂O and 70 % N₂. In this report, the flue gas with such a composition is referred to as "standard flue gas" from here on. The O₂ and CO₂ contents in flue gas flow are measured with an electrochemical analyser (SONOX Rend-O-meter) which is calibrated before the systematic measurements. The H₂O content is estimated as two times content of CO₂ assuming that pure methane is burned. To observe the influence of gas composition on the removal of SO₂ and NO, the O₂, CO₂ and H₂O contents in flue gas can be varied by adding excess air. In this system, a increase of O₂ content naturally causes a decrease of CO₂ content. The change of total gas flow through the reactor also causes a change of gas temperature. The pollutant gases of NO, SO₂ and NH₃ gases are introduced from gas cylinders through calibrated mass flow controllers. Before the measurements, the mass flow controllers are calibrated with gas analyser for NO in flue gas and for SO₂ in air. Afterwards, the mass flow controller for NH₃ is calibrated with the thermal-reaction of SO₂-NH₃ in room air. In the calibration of gas flow controller of NH₃, much high concentration of SO₂ is used. The amount of the injected NH₃ is calculated as two times the concentration of removed SO₂ when no slip of NH₃ can be see from the UV absorption spectra. We believe that this method is valid because the NH₃ absorption is easily seen from the UV spectra at 213.4 nm or 204 nm. The accuracy of NH₃ flow controller is estimated as the sum of the accuracy of SO₂ (3 %) and total flow measurement (2 %). In this way, the system error for gas detection can be reduced to a minimum. With flow controllers, NO and SO₂ are usually injected with an initial concentration of about 300 ppm (with 10 ppm maximum deviation) and in most cases the amount of NH₃ injection is less than its stoichiometric value of 900 ppm (with 45 ppm deviation or less). A flue gas composition like this is realistic for a power plant combusting low-sulphur coal. In our cleaning process with NH₃ injection, SO₂, NO and NH₃ are detected by UV absorption at the exit of the system. In the absence of NH₃ injection, SO₂ and NOₓ (i.e. NO+NO₂) and NO are detected using an electrochemical analyser.

2.2 Pulse power supply

The electrical pulses used in the experiments are created with a triggered spark gap switched capacitor, see figure 2. Two examples of voltage and current wave shapes are given in Fig.3. With the aid of HV transformer, up to 70 kV voltage pulse can be output with a rise time of about 100 ns and a half-width of 180 ns. Due to the large inductance of the transformer, the maximum pulse voltage rise rate is about 0.7 kV/ns and the tail of the voltage pulse has a long and decayed oscillation. The half-width of corona current pulse is 140-150 ns. This is almost four times higher than the streamer transition time of 30-40 ns [4]. One should bear in mind that the parameters of pulses used here are not the optimum values for this electrode system [4]. A dc bias voltage up to 30 kV can be added to corona wire which leads to higher current pulses and higher input discharge energy. The supply can be operated up to 250 Hz. The electrical energy input into the corona discharge is usually varied by changing of the pulse frequency. The pulse voltage is measured with a capacitive-resistive divider (Tek. P6015) with a division ratio 1/1000. The current pulse is measured with a Rogowsiki coil (Pearson model 2877, inner diameter 6 mm, rise time 2 ns). Both the voltage and current pulses are detected with a digital oscilloscope with 300 MHz analogue bandwidth and 2 ns sample time (Tek.DSA 601). Data are transmitted from the oscilloscope to a
computer via a GPIB interface. The total power per pulse can be calculated by multiplying the current and voltage waveforms. The associated discharge energy is obtained by the interruption of the power and the subtracting the capacitive energy of the electrode arrangement. The measurements of the electrical energy input with high time resolution have been described in more detail elsewhere[8]. The energy cost $W_m$ (in unit of eV/molecule) of the cleaning process is calculated from the specific discharge energy $E$ (in unit of Wh/Nm$^3$) and the amount of removed molecules $\Delta N$ (in unit of ppm):

$$W_m = \frac{897 E}{\Delta N}$$

Figure 2: The electrical circuit for the production of HV pulses with a dc bias.

Figure 3: Two examples of voltage and current wave shapes.

(a) $V_{dc}=20 \text{ kV}$, $V_p=70 \text{ kV}$, $f=100$ Hz; Per single pulse: $Q_{off}=9567 \text{ nC}$, $Q_{on}=9438 \text{ nC}$ (98.6%), $E_{tot}=510 \text{ mJ}$, $E_{on}=507 \text{ mJ}(99\%)$. (b) $V_{dc}=0.0 \text{ kV}$, $V_p=66 \text{ kV}$, $f=50$ Hz; Per single pulse: $Q_{off}=6318 \text{ nC}$, $Q_{on}=5869 \text{ nC}$ (93%), $E_{tot}=412 \text{ mJ}$, $E_{on}=410 \text{ mJ}$ (99.6%).
2.3 UV absorption set-up

A UV absorption system is located at the exit of the cleaning set-up for the gas detection (fig.1). Figure 4 is the diagram of UV absorption system. The light source used in this system is a high pressure Xe lamp with 0.5 J input energy per pulse. With a lens with a focal length of 20 cm in front of the lamp a parallel light beam is produced.

After passing through the gas absorption cell of 1.53 m in length, the light is focused with the second lens (f = 20 cm) onto the entrance slit of a 0.5 m Jarrel Ash monochromator (slit width: 50 mm). The light is detected at the output slit with a Hamamatsu R666 Photomultiplier (PM) with GaAs cathode. The PM is operated at -830 V in the scan of 200-237.5 nm and -600 V in the scan of 280-320 nm, respectively. The electrical signal (0-2V) from the PM is digitised by a 12-bit analogue-to-digital converter and read out by a microcomputer. A spectral scan of 200-237.5 nm takes 3 mins and yields 3276 points. The collected data is analysed using the well-known modified Beer-Lambert law:

$$I(\lambda) = I_0(\lambda) \exp(-\sigma(\lambda)C L)$$

where $I_0$ and $I$ are the light intensities with and without absorption, while $\sigma(\lambda)$ denotes the absorption cross section of a gas at wavelength $\lambda$, $C$ the concentration of measured gas and $L$ the optical path length of the absorption cell. $I_0$ is calculated at wavelength $\lambda$ using linear curve-fitting.

3. UV absorption measurements

3.1 Absorption spectra

SO₂, NO and NH₃ have several strong absorption bands in the ultraviolet region of the spectrum. These features in principal can be exploited to measure gas concentrations in flue gas cleaning process. But we have observed that a variety of factors influences absorption measurements, including:

1. the presence of mist, water vapour and particles in the path cause light absorption and light
scattering which give rise to a complex, unstable absorption spectrum and therefore to cause
difficult to accurately measure $I_p$;
(2) the cross sections for NO and NH$_3$ are concentration-dependent (see calibrations);
(3) the saturation of the absorption bands with increasing concentration;
(4) a gas mixture with SO$_2$, NO and NH$_3$ leads to overlap of absorption bands;

In order to avoid the particles and aerosol entering into absorption cell, an electrostatic
precipitator is installed before the absorption cell. The absorption cell is heated over 100$^\circ$C to
avoid the occurrence of water condensation.

**Figure 5:** NO absorption spectra in 80$^\circ$C flue gas flow.

![NO absorption spectra](image)

(a) In the region of 200-230 nm NO presents three strong absorption bands at 205 nm, 214.5 nm
and 226.2 nm. (b) UV absorption at 226.2 nm using four values for the concentration of NO.

**Figure 6:** SO$_2$ spectrum in 65$^\circ$C air flow.

![SO$_2$ spectrum](image)

(a) Fine structure at 290-310 nm. (b) The absorption near 300 nm for four values of SO$_2$ concentra-
tion.
Figure 7: NH₃ spectrum in 70°C air flow with intentional injection of 10 ppm NO.

(a) in the region of 200-230 nm, absorption maximum at around 204 nm, 209 nm, 213 nm, 217 nm and 222 nm.

(b) NH₃ absorption spectra at around 213.4 nm for 0-435 ppm.

(c) NH₃ absorption spectrum at around 221.6 nm for 435-1050 ppm.

Figure 8: 67 ppm NO₂ absorption spectra in the region of 425-450 nm in 80°C air flow with corona discharge. It's too weak to be detected with reasonable accuracy.
In the region of 200-230 nm NO presents three strong absorption bands at 205 nm, 214.5 nm and 226.2 nm as shown in figure 5(a). In fig.5(b), the NO absorption of (0,0) gamma-band located at 226.2 nm is shown using four values for the concentration of NO. With increasing concentration of NO, it is observed that absorption at 205 and 214.5 nm are readily saturated as compared with that at 226.2 nm. In order to obtain a high measurement accuracy in the range of 0-450 ppm, absorption band at 226.2 nm is employed for NO detection. SO₂ presents a very broad spectrum with a fine structure in 290-310 nm, as shown in fig.6(a). The absorption maximum around 300 nm is used for SO₂ detection. The absorption around 300 nm are shown in fig.6(b) for four values of SO₂ concentration. The leak NH₃ at the exit of the system is specially included in our measurements. The ammonia spectrum in the region of 200-230 nm exhibits absorption maxima at around 204 nm, 209 nm, 213 nm, 217 nm and 222 nm as shown in fig.7(a). In fig.7(b) and (c) give the NH₃ absorption spectra in the room air flow at around 213.4 nm and 221.6 nm, respectively. At relatively long wavelength absorption occurs at high concentration while the saturation occurs at the shorter wavelength. This leads to the most accurate detection of NH₃ below 450 ppm at 213.4 nm and for 400-1000 ppm at 221.6 nm. Because the UV absorption of N₂O is too weak, as shown in Fig.8 for the spectra of 67 ppm, NO₂ can not be detected with reasonable accuracy using UV absorption. In the absence of NH₃ injection, a electrochemical analyser is used to detect NO. In the presence of NH₃, only NO is detected using UV absorption.

3.2 Calibrations

In principle, gas concentration can be calculated using the absorption cross sections. Unfortunately, data of UV absorption cross sections for NO, SO₂ and NH₃ are limited. The most reported in the literature are the total absorption values which are generally higher than the differential ones. In view of this obstacle, the calibration is directly assessed by comparing the results with an electrochemical analyser for NO and SO₂, and calibrated gas flow controllers for NH₃. Since a part of NO spontaneously converts into NO₂ in air, NO calibration is made only with flue gas. For SO₂ and NH₃, the calibrations are made with air to avoid reactions with water. It can be seen, in fig.9, the absorption (oC(m⁻¹)) of NO at 226.2 nm and NH₃ at 213.4 nm strongly depends on the concentrations while NH₃ at 221.6 nm and SO₂ at 300 nm present almost linear absorption-concentration relationships. For signal NO, SO₂ and NH₃ gas with 0-450 ppm(a) and 0-1200 ppm(b) injected in flue gas or air flow, the calibration curves are given in fig.9. The measurements of NO and SO₂ have an error of less than 3% (or 10 ppm for 300 ppm whichever is the highest). For ammonia it is slightly higher with 5% at 900 ppm, but concentrations down to 1 ppm can be observed at 204 nm.

![Fig 9: Calibrations of NO, SO₂ and NH₃ at lower (a) and higher (b) concentrations.](image-url)
A problem in gas mixture is the overlap of SO$_2$ absorption with NH$_3$ and NO in the region 200-237.5 nm (Fig.10). To overcome this problem, the SO$_2$ fractional absorption is subtracted from the overlap at the wavelengths for NO and NH$_3$ detection, respectively, since SO$_2$ is firstly detected at around 300 nm without this difficulty. Additional errors caused by this cross calibration are negligible. Fig.11 gives SO$_2$ concentration-absorption calibrations at 213.4 nm and 221.6 nm. It can be seen that when SO$_2$ concentration is less than 25 ppm, there is actually no overlap at 226.2. Besides the influence factors mentioned above, other possible factors are also examined. The total gas flow and the stability of Xe-lamp signal used in the cleaning measurements have no apparent influence on the measurement. But, during the following experiments, the temperature in absorption cell, the settings of monochrometer and PM should be fixed at the values used in the calibrations. The absorption measurement must be corrected to account for the difference between calibration and experiment temperatures of the gas flow in the reactor using the ideal gas law.

Figure 10: SO$_2$ absorption spectrum in the region of 212-220 nm (a) and 222-230 nm (b) for four concentrations.

Figure 11: Cross calibrations of SO$_2$ absorption at 226.2 nm for NO detection and 213.4 nm for NH$_3$ detection.
4. Cleaning measurements

4.1 Removal of NO/NOx

4.1.1 DC bias effect

For optimizing the energization, the effect of dc bias on the removal of NO and NOx (the sum of NO+NO2) energy efficiency is firstly investigated in flue gas at 130 °C and 25 Nm3/h (9.6 s residence time) with 3 % O2, 10 % CO2 and about 20 % H2O. The initial NO/NOx concentrations are 350 and 380 ppm, resp. Test results are graphically presented in Fig. 12. It can be clearly seen that both NO and NOx removal performance is better with 20 kV bias than that with 30 kV bias at the same energy input. For instance, at 6 Wh/Nm3 energy input, about 38% NO and 23% NOx (energy cost: 40 eV/NO, 61 eV/NOx) are removed in the case of 20 kV dc bias but only 30% NO and 18% NOx (energy cost: 50 eV/NO, 76 eV/NOx) in the case of 30 kV dc bias.

Figure 12: Comparison of NO/NOx removal at 20 kV and 30 kV bias.
\(T=130 \, ^\circ C, \, t_{res}=10 \, s, \, flow=25 \, Nm^3/h, \, [NO]=350 \, ppm, \, [NOx]=380 \, ppm, \, O_2=3 \, %, \, CO_2=10 \, %\)

In 80 °C flue gas (12 % O2; 2.5 % CO2) with 15 s residence time, the performance of NO/NOx removal at 30 kV bias is compared with 15 kV dc bias in Fig. 13. The initial NO/NOx concentrations are 330 and 360 ppm, respectively. At about 5.3 Wh/Nm3, the removal rate with 15 kV bias is almost two times higher than that with 30 kV. Correspondingly, the energy cost is reduced a factor two at the same removal rate.

Figure 13: Comparison of NO/NOx removal at 15 kV and 30 kV bias.
\(T=80 \, ^\circ C, \, t_{res}=15 \, s, \, flow=15 \, Nm^3/h, \, [NO]=330 \, ppm, \, [NOx]=365 \, ppm, \, O_2=12 \, %, \, CO_2=2.5 \, %\)
In 70 °C standard flue gas with 30 s residence time, the removal performances of NO/NO<sub>x</sub> with and without dc bias are compared in fig. 14. The better results have been obtained in the absence of a bias.

**Figure 14:** Comparison of NO/NO<sub>x</sub> removal at 0 kV and 20 kV bias in standard flue gas. 
(T= 70 °C, t<sub>res</sub>=30s, flow=9 Nm<sup>3</sup>/h, [NO]<sub>i</sub>= 300 ppm, [NO<sub>x</sub>]<sub>i</sub>=325 ppm.)

In 80 °C flue gas with standard composition at a gas residence time of 30 s, the relationships of energy cost vs. dc voltage in the case of the removal of 32 % NO and 15 % NO<sub>x</sub> are measured. The initial concentrations of NO and NO<sub>x</sub> are 330 ppm and 360 ppm, respectively. As shown in fig. 15(a), the energy cost for removal of both NO and NO<sub>x</sub> increase slightly with the increase of dc voltage up to 20 kV (The dc corona inception voltage of this electrode system is around 18 kV). Beyond 20 kV, this increase becomes stronger. The energy consumption per removed NO or NO<sub>x</sub> at 30 kV is almost a factor two higher than that at 20 kV. In the case of 50 % NO removal, a difference is increased a factor three at a gas residence time of 15 s. This result is contrary to data obtained by Belousova<sup>[10]</sup>. Figure 15(b) shows the effects of dc bias on the injection energy and chargers of the corona discharge per pulse and discharge power. It is evident that the general trend of all curves in both figures presented are almost the same. This indicates that the use of dc bias mainly increases the discharge energy input, but certainly above the inception voltage this additional energy is not used efficiently and therefore leads higher energy cost for NO/NO<sub>x</sub> removal. This finding is of practical importance for optimizing the energization.

**Figure 15:** Effect of dc bias on the removal of about 32 % NO and 15 % NO<sub>x</sub> in standard flue gas (T=80 °C, t<sub>res</sub> = 30 s, flow= 9 Nm<sup>3</sup>/h, [NO]<sub>i</sub>= 330 ppm, [NO<sub>x</sub>]<sub>i</sub>=360 ppm).
4.1.2 Residence time effect

In 70 °C standard flue gas with 300 ppm NO injection (320 ppm NO\textsubscript{2}), the NO/NO\textsubscript{2} removal is respectively tested at the residence time of 6 s and 30 s with 20 kV dc bias. The results are plotted in fig.16. Due to the power limitation of the supply, the removal rate at 6 s can not be compared with that at 30 s at the same energy input. But, with a curve-fitting, all data points are located on one smooth curve. This implies that the removal performances have no apparent difference between both cases. At 80 °C standard flue gas with 320-330 ppm NO injection, the results of NO removal at the residence time of 30 s and 15 s are compared in fig.17 with 15 kV and 20 kV dc bias, respectively. An apparent difference is found for removal rates with both residence times at same dc bias. The removal performance at 15 s is better than that at 30 s.

Figure 16: NO/NO\textsubscript{2} removal in standard flue gas with the residence time of 6 s and 30 s.
(T=70 °C, [NO]\textsubscript{i}=300 ppm, [NO\textsubscript{2}]\textsubscript{i}=320 ppm, \textit{V}\textsubscript{dc}=20 kV)

Figure 17: Comparison of NO removal in the standard flue gas with the residence time of 15 s and 30 s.
(T=80 °C, [NO]\textsubscript{i}=330 ppm)
In order to clarify the effect of residence time on the removal performance, the further measurements are conducted for 30% removal of 320-330 ppm NO with dc voltage of 15 kV and 20 kV, respectively. In this case, the standard flue gas with 80 °C is used. The input of discharge energy is varied with the change of the pulse frequency. As shown in fig.18, the required energy for 30% NO removal first goes down with increasing residence time. When reaching a minimum at around 15 s, the energy goes up. In the period of 30-60 s, this specific energy is almost the same as that at 6 s. At 15 s residence time, the energy cost for the NO removal can be at least reduced by 30% in both cases of 15 kV and 30 kV dc bias. But, the required energy at 15 kV is 25% less than that at 30 kV. In the region of the longer residence time, the higher energy requirement could be explained by the formation of NO due to reverse reaction of NO₂ and radical O which offsets the NO reduction. For the shorter residence time, the conversion of 30% NO requires active radicals and therefore needs more energy input, which has been confirmed by using chemical kinetics calculations [10]. This result suggests that there is a optimum residence time for the removal of NO/NO₂ in a certain volume of the discharge reactor.

Figure 18: Effect of gas residence time on the removal of about 30% NO in the standard flue gas. (T=80°C, [NO]=330 ppm). The optimal residence time is around 15 s.

4.1.3 O₂ and H₂O effect

The flue gas used in most cases has 6% O₂ and 16% H₂O. It has known that the O₂ and H₂O contents have a pronounced influence on the removal of NO/NO₂. In the present experiments, this effect is also examined in 80 °C flue gas with 15 s residence time. The initial concentration of NO/NO₂ are 330 and 360 ppm, respectively. The removal performance in the flue gas with 6% O₂ and 16% H₂O are compared with that in the flue gas with 12% O₂ and 10% H₂O in Fig.19. The effect of CO₂ content on the removal of NO/NO₂ is small. As seen in fig.19, when the total content of O₂ and H₂O is the same, the removal rate at 12% O₂ content is better than that at 6% O₂. In the region of energy input in fig.19 with 15 kV ac bias, the removal rate of NO/NO₂ are improved about 30%. This is in general in agreement with the earlier small-scale measurements by Tas [11]. Since a real flue gas has a O₂ content of around 6%, the removal of NO/NO₂ can not been further optimized with gas composition.
Figure 19: Effect of $O_2$ and $H_2O$ on the removal of $NO/NO_x$ in the case of same total content (22%) of $O_2$ and $H_2O$.

$\{T=80^\circ C, t_{res}=15\ s, flow=19\ Nm^3/h, [NO]=330\ ppm, [NO_x]=360\ ppm, V_d=15\ kV\}$. The removal rate at 12 % $O_2$ content is better than that at 6 % $O_2$.

4.1.4 Temperature effect

$NO/NO_x$ removal experiments are performed with a dc bias of 30 kV, respectively. At 130 °C, the flue gas conditions are: 3 % $O_2$, 20 % $H_2O$, 9.6 s residence time, 350 ppm NO and 380 ppm $NO_x$. At 80 °C, these are :10 % $O_2$, 12 % $H_2O$, 16 s residence time,320 ppm NO and 360 ppm $NO_x$. Although the gas conditions are not the same in 130 °C and 80 °C flue gases, the apparent influence on the NO/NO$_x$ removal performance in fig. 20 are believed to be mainly ascribed to the gas temperature. At 80 °C, more than 90% NO is removed when 11 Wh/Nm$^3$ discharge energy is input, resulting in a energy cost of less than 35 eV/NO. In comparison with the results at 130 °C, this is almost a factor two better. The temperature dependence presented here is consistent with the previous work at EUT [4]. In combination with earlier work, it suggests that the optimum gas temperature for NO/NO$_x$ removal is just above the condensation point of water.

Figure 20: Temperature effect on the removal of $NO/NO_x$.

(flue gas 1: $T=80^\circ C$, $t_{res}=16s$, $[NO]=320\ ppm$, $[NO_x]=350\ ppm$, $O_2=10\ %$, $H_2O=12\ %$;
flue gas 2: $T=130^\circ C$, $t_{res}=10s$, $[NO]=350\ ppm$, $[NO_x]=380\ ppm$, $O_2=3\ %$, $H_2O=20\ %$).

The lower temperature is better for removal of NO and $NO_x$.
4.2 Removal of SO₂

The SO₂ removal tests are conducted in room air and flue gas, and in the cases with and without NH₃ injection, respectively.

4.2.1 Removal of SO₂ in air

In air of 24 °C and 23 % RH, 300 ppm SO₂ was introduced into a 22.4 Nm³/h air flow. As shown in Fig. 21, SO₂ removal rate is only 10-30 % by the corona discharge alone. At 7.2 Wh/Nm³ energy input, 480 ppm NH₃ injection produces 55 % SO₂ removal rate and no slip NH₃ was observed. At 8 Wh/Nm³, 600 ppm NH₃ injection produces 88 % SO₂ removal rate and no slip NH₃ was observed. In the case of 600 ppm NH₃, SO₂ removal rate goes through a maximum of 90 % at 1.6 Wh/Nm³ and then starts to slightly go down with increasing power density. But slip NH₃ is always decreasing with increasing power density. The removal results of SO₂ obtained here are in agreement with the those obtained by Chang J. S. [12].

Figure 21: The removal of SO₂ in air flow with and without addition of NH₃, 
(T=24 °C, tₚ=14s, flow =22 Wh/Nm³, RH=23%, [SO₂]=300ppm).

Figure 22: Comparison of the removal of SO₂ in presence of NH₃ in air without and with discharge. 
(T=70 °C, tₚ=14s, flow=19 Nm³/h, [H₂O]=16%, [SO₂]=300ppm).

The auto-thermal reaction is dominant for SO₂ removal.
In 70 °C air with 300 ppm SO₂, the removal rates are compared in the cases with and without discharge energy input for the injection NH₃ concentration of 480 ppm, 600 ppm and 720 ppm. This measurements show several trends. The first is that more NH₃ injection leads to higher SO₂ removal rate, both with and without discharge. A clear trend in the leak NH₃ is that the discharge reduces the leak of NH₃. Thirdly, thermal reaction without discharge can remove 36-58% of 300 ppm SO₂ in air, also depending on the amount of NH₃ injection.

4.2.2 Removal of SO₂ in flue gas

The removal of SO₂ is also tested in a wide region of gas condition (H₂O: 1-16 %, Temp.: 24-130 °C, NH₃: 480-720 ppm). Without NH₃ injection SO₂ removal rate is never more than 30 % at energy input upto 10 Wh/Nm³ in both air and flue gas. But, in the case of NH₃ injection, SO₂ removal significantly increases with the increase in the amount of NH₃ (fig.24). The gas temperature and water content have an obvious influence for SO₂ removal with NH₃ injection. At 76 °C and 16 % H₂O, more than 99% SO₂ removal rate is achieved at 3 Wh/Nm³ with 720 ppm NH₃ injection. In flue gas, it is also observed that the corona discharge hardly improves the SO₂ removal, but strongly reduces NH₃ slip. Slip of NH₃ also increases with increasing NH₃ concentration. SO₂ removal by thermal reaction of SO₂-NH₃ without discharge is much more effective than that by energized corona process in air and flue gas, but slip NH₃ is much higher in the thermal reaction. These experiments indicate that the high discharge energy is required for complete NH₃ removal. This is quite similar to the results of Civitano [3].

Figure 23: The removal of 300ppm SO₂ in a wide condition region (H₂O: 1%-16%, T: 24-130 °C) without NH₃ injection. SO₂ removal rate is never more than 30% at energy input upto 10 Wh/Nm³.

Figure 24: Effect of NH₃ injection on the removal of 300 ppm SO₂ in flue gas (1: T=76°C, t_res =6 s, H₂O = 16 %, E = 3 Wh/Nm³; 2: T=94 °C, t_res =12 s, H₂O=8 %, E = 6 Wh/Nm³; 3: T=94°C, t_res =12 s, H₂O=3 %, E=7 Wh/Nm³).
4.2.3 History effect

During the SO$_2$ removal experiments with NH$_3$ injection, it is observed that the SO$_2$ removal has a strong history effect. Two typical sets of tests are shown in fig.25. In the case of 720 ppm NH$_3$ injection into gas flow with a gas temperature of 90 °C and a gas residence time of 12 s, the test is started at 7 Wh/m$^3$ after 10 mins. This time is a little longer than the time required by the gas to flow through the whole system and reach the absorption cell. It is observed that the SO$_2$ removal rate increases from 70% at 7WhNm$^3$ with a decrease of the energy input. At 1.9 Wh/Nm$^3$, a 84% SO$_2$ removal rate is obtained. Then the corona is off, the removal rate goes down to 74%. The leak NH$_3$ always decreases with increasing energy input. In the second set of tests, a flue gas of 70 °C and a gas residence time of 30 s is used. The tests are started 1.5 h after 600 ppm NH$_3$ is injected. The time interval between two data points is 20 mins for each increase of energy input. In this procedure, the SO$_2$ removal rate always increases with the more energy input. At 7.7 Wh/Nm$^3$, a 97% removal of 300 ppm SO$_2$ is detected. The NH$_3$ slip also decreases from 17 ppm to less than 1 ppm. History effects like this are also reported by Li [13].

Figure 25: History effect for the removal of SO$_2$ in flue gas.

- 5: $T=70 ^\circ C$, $t_{res} = 30$ s, $H_2O=18\%$, $[NH_3]= 600$ ppm;
- 2: $T=94 ^\circ C$, $t_{res} = 12$ s, $H_2O=3\%$, $[NH_3]= 720$ ppm

The arrow indicates the time sequence of the data points. History effect is beneficial for SO$_2$ removal.

4.3 Combined removal of NO and SO$_2$

4.3.1 SO$_2$ effect on DeNO/DeNO$_x$

The effect of SO$_2$ injection on the NO/NO$_x$ removal is tested in a 70 °C flue gas with a residence time of 30 s. The results obtained at an energy input of 7 Wh/Nm$^3$ is plotted in fig.26. In this case, a 20 kV dc bias and 350 ppm NO$_x$ (320 ppm NO) are used. NO removal rate is 52% without SO$_2$ injection, resulting in 40 eV/NO. In this case, the reduction of NO$_x$ is 37 % (50 eV/NO$_x$). When SO$_2$ is introduced into the gas flow, NO and NO$_x$ removal rates are enhanced. At 900 ppm SO$_2$, NO and NO$_x$ removal rates increase to 78 % and 71 %, respectively, corresponding to energy cost of 24 eV per removed molecule for both NO and NO$_x$. By comparing figure 27(a) with figure 13-14, it is noted that in the presence of SO$_2$ the improvements of the removal NO$_x$ is much stronger. This implies that SO$_2$ can reduce the reverse reaction in the removal of NO$_x$. 

18
4.3.2 Synergetic effect of \( \text{SO}_2 \), \( \text{NO} \) and \( \text{NH}_3 \)

It is also found that NO concentration decreases from 308 to 260 ppm with 600 ppm \( \text{SO}_2 \) injection without corona discharge. However, NO concentration goes back in this case to its initial value when 1200 ppm \( \text{NH}_3 \) is also injected. With corona discharge, the \( \text{NH}_3 \) and \( \text{SO}_2 \) injection enhance the NO conversion, respectively but also together. The typical results in 70 °C flue gas with 6 s residence time is graphically presented in Fig. 27. It can be seen that 300 ppm \( \text{SO}_2 \) injection improves NO removal with a factor three. 600 ppm \( \text{NH}_3 \) injection improves NO removal with a factor two, but leak \( \text{NH}_3 \) is quit high (190 ppm at 3 Wh/Nm\(^3\); 280 ppm at 2.7 Wh/Nm\(^3\)). The positive effect of \( \text{NH}_3 \) on NO removal is in good agreement with recent results of Chang [12] and Niessen [14]. When \( \text{SO}_2 \) and \( \text{NH}_3 \) are simultaneously introduced into gas flow, the enhancement of NO removal rate is about 1.5, which is lower than in the case of respective injection of \( \text{SO}_2 \) and \( \text{NH}_3 \). Without \( \text{NH}_3 \) injection, \( \text{SO}_2 \) removal rate is 22-25 % at energy input of 1.5-2.5 Wh/Nm\(^3\). NO presence has a small positive effect on \( \text{SO}_2 \) removal. In the presence of \( \text{NH}_3 \), but without NO injection, 90 % \( \text{SO}_2 \) removal rate is obtained at 1.5 Wh/Nm\(^3\) with 5 ppm \( \text{NH}_3 \) slip. When three species exist together, \( \text{SO}_2 \) removal rate is more than 99 % with leak \( \text{NH}_3 \) of 5-13 ppm. Leak \( \text{NH}_3 \) is less with more energy input.
4.3.3 NH₃ effect on the removal of SO₂ and NO

In 70 °C standard flue gas with 6 s residence time, the effect of NH₃ injection on the removal of NO (300 ppm) and SO₂ (300 ppm) is investigated. As shown in fig. 27(b), the SO₂ and NO removal rates increase with increasing NH₃ injection. When NH₃ concentration increases from 600 to 900 ppm at about 2 Wh/Nm³, the NO removal rate increases from 25 % to 50 %, correspondingly leads to a decrease of energy cost from 26 eV/NO to 12 eV/NO. But, in this case, the leak NH₃ also increases with increasing NH₃ injection (5 ppm at 600 ppm injection; 140 ppm at 900 ppm injection).

![Figure 27(b): Effect of NH₃ injection on the simultaneous removal of SO₂ and NO in standard flue gas (T~70 °C, tₘ~6 s, [NO]₀=300 ppm, [SO₂]₀=300 ppm, V₆~20 kV)](image)

4.3.4 Enhancement of synergetic effect

In order to effectively use the positive effect on NO removal, NH₃ is injected at the location of 70 cm from the exit of the corona reactor (location 2 in fig. 1). The results at 80 °C flue gas with 30 s residence time is plotted in fig. 28. SO₂ from 300 to 1000 ppm is injected with corresponding stoichiometric NH₃ of 600-2000 ppm. NO concentration is 320 ppm. Energy input is 7 Wh/Nm³ with 15 kV dc. It is seen that NO removal rate increases with SO₂ and NH₃ concentration. When

![Figure 28: Removal of SO₂ and NO from standard flue gas in the case of NH₃ injection later (T~80 °C, tₘ~30 s, [NO]₀=320 ppm, [NH₃]₀=2[SO₂]₀, E=7 wh/Nm³, V₆=15 kV).](image)

NO removal of 81% (23 eV/NO) and SO₂ removal of over 98% with less than 5 ppm leak NH₃ have been obtained.
SO₂ concentration reaches 600 ppm, NO removal rate increases from 61 % (without SO₂ and NH₃ injection) to 81 %. Correspondingly energy cost reduces from 37 to 23 eV/NO. The further increase of SO₂ and NH₃ does not give a further increase of NO removal. In this set of measurements, SO₂ removal rate is always over 98% and leak NH₃ is always less than 5 ppm.

When 300 ppm SO₂ is injected at the location of 70 cm (location 2 in fig.1) form the reactor exit and NO (320 ppm) and NH₃ (changed from 600-1200 ppm) are injected before the reactor (location 1 in fig.1), the NO removal is also improved at 7.5 Wh/Nm³ as shown in fig. 29. The removal rate of 97 % for SO₂ and 81 % for NO (25 eV/NO) are obtained at 900 ppm NH₃ injection. The leak NH₃ is only about 2 ppm.

Figure 29: Removal of SO₂ and NO from standard flue gas in the case of SO₂ injection later. (T=80 °C, t₀=30 s, [NO]=320 ppm, [SO₂]= 300 ppm, E = 7.5 Wh/Nm³, V_d=15kV).

The removal rate of 97 % for SO₂ and 81 % for NO (25 eV/NO) with 2 ppm leak NH₃ are obtained at 900 ppm NH₃ injection.

In the case of 15 s gas residence time and 3.7 Wh/Nm³ energy input with 15 kV dc bias, the effect of NH₃ injection before the reactor is plotted in fig. 30. Without SO₂ injection, 300 ppm NH₃ injection improves NO removal with a factor two and a half, i.e., removal rate increases from 31 % without NH₃ injection to 73 % with NH₃ injection, resulting in a decrease of energy cost from 32 to 14 eV/NO.

Figure 30: Effects of NH₃ and/or SO₂ injection (later) on the removal of NO from the standard flue gas. (T=80 °C, t₀=15 s, flow = 19 Nm³/h, E = 3.7 Wh/Nm³, V_d=15 kV).

NH₃ injection improves NO removal rate from 31 % to 73 % (14 eV/NO) with 1.3 ppm leak NH₃, SO₂ and NH₃ together improves NO removal rate to around 68 % (15 eV/NO).
Leak $\text{NH}_3$ increases from 1.3 to 31 ppm with increasing $\text{NH}_3$ concentration from 300 to 600 ppm. When 600-1200 ppm $\text{NH}_3$ and 300 ppm $\text{SO}_2$ are injected simultaneously but at different locations, this improvement for NO removal becomes a little smaller. The NO removal rate is around 68 % in this case, corresponding to a energy cost of 15 eV/NO. $\text{SO}_2$ removal rate is always more than 99 % and leak $\text{NH}_3$ increases from less than 1 ppm to 13 ppm with increasing the injection of $\text{NH}_3$. As compared with the results in fig.27, the positive effect of $\text{SO}_2$ and $\text{NH}_3$ together on NO removal is greatly enhanced with the adjusting the locations of gas injections. In this case, it is interesting to find that the NO and $\text{SO}_2$ concentrations at the exit of the system change with the measurement time. At 3.7 Wh/Nm$^3$ energy input, the NO concentration firstly goes down to a minimum of 30 ppm (92 % removal) at 20 mins and then goes up to a maximum of 120 ppm (63 % removal). After 50 mins, the NO concentration reaches a stable level of around 105 ppm (68 % removal, 15 eV/NO). $\text{SO}_2$ and $\text{NH}_3$ concentrations always decrease with the time. After 50 mins, almost 100 % $\text{SO}_2$ is removed without $\text{NH}_3$ slip. At 4 Wh/Nm$^3$ energy input, a same change in trend for NO and $\text{SO}_2$ concentrations is observed. The stable level is at 50 ppm NO (85 % removal, resulting in 12.6 eV/NO). The 95 % of 300 ppm $\text{SO}_2$ is finally removed with less than 3 ppm $\text{NH}_3$ slip. This is up to now our best result. Such a time-dependence of the removal of $\text{SO}_2$ and NO with $\text{NH}_3$ injection is probably related to the formation of particles and heterogeneous reactions. The results presented from fig.28 to fig.31 indicates that the $\text{NH}_3$ and $\text{SO}_2$ injections at the different location on the reactor is beneficial for the improvement of energy efficiency of NO removal.

Figure 31: The variation of NO and $\text{SO}_2$ concentration with the measurement time. (T=80 °C, $t_{\text{res}}$=15 s, standard flue gas, $\text{SO}_2$ injection later, $[\text{NO}]_i=330$ ppm, $[\text{SO}_2]_i=300$ppm, $[\text{NH}_3]_i=600$ ppm, $V_{de}=15$ kV).

85% NO (12.6 eV/NO) and 95% $\text{SO}_2$ is finally removed with less than 3 ppm $\text{NH}_3$ slip at 4 Wh/Nm$^3$.

5. Two-stage cleaning measurements

5.1 NO and NO$_x$ removal

With two corona reactors in series, the experiment on DeNO/DeNO$_x$ is conducted in 70 °C standard flue gas with 300 ppm NO (320ppm NO$_x$) and 30 s residence time (18 Nm$^3$/h flow). The results are plotted in fig. 32 in comparison with the results obtained in single-stage at the same residence time (30 s, 9 Nm$^3$/h flow) and same gas conditions. As seen in fig.32, the removal rates of NO and NO$_x$ in two-stage are a factor two lower than that in single-stage at the same discharge power input. But, the energy costs of NO and NO$_x$ removal in both cases are almost the same since the specific energy (in unit Wh/Nm$^3$) also decreases a factor two in the two-stage. When the residence time in the two-stage system is increased to 60 s, no apparent difference is found for NO and NO$_x$ removal.
Figure 32: Comparison of the removal of NO and NOₓ with single-stage and double-stage in the standard flue gas ($T=70 \, ^\circ C, t_{\text{res}}=30 \, s, [\text{NO}]_{1}=300 \, \text{ppm}, [\text{NO}]_{2}=320 \, \text{ppm}, V_{\text{dc}}=20 \, \text{kV}$).

The removal rates of NO/NOₓ in two-stage system are a factor of two lower than that in single-stage system at the same discharge power.

5.2 Combined removal of SO₂ and NOₓ

The double-stage measurements of simultaneous removal of SO₂ (300 ppm) and NO (310 ppm) in the presence of NH₃ (600 ppm) are carried out in a 70 °C flue gas with a residence time of 30 s. The flow velocity is about 10 m/min, resulting in an interruption time of 5 s in-between two chambers. As compared with one-stage measurements with the same gas residence time, the NO removal rate in the two-stage is a factor of two lower than that in the single-stage. As given in Fig.33, at about

Figure 33: Comparison of NO removal with single-stage and double-stage in the standard flue gas in presence of NH₃ and SO₂ ($T=70 \, ^\circ C, t_{\text{res}}=30 \, s, [\text{NO}]_{1}=300 \, \text{ppm}, [\text{SO₂}]_{1}=300 \, \text{ppm}, [\text{NH₃}]_{1}=600 \, \text{ppm}, V_{\text{dc}}=20 \, \text{kV}$).

The NO removal rate in the two-stage is a factor of two lower than in the single-stage.

70W power input, the NO removal rate are 82 % and 45 % for single and double stage treatments, respectively, resulting in about 25 eV/NO for both. This is similar to that without SO₂ and NH₃ injection. When NH₃ is injected in-between stages (location 3), the performance of NO removal rate is improved as well as energy efficiency. At 70 W power input, NO removal rate is 58 %, corresponding to an energy cost of 22 eV/NO. But, in general, the NO removal rate is still lower than that in single-stage with the same energy input. This is quite different from the result using electron-beam irradiation.
6. Removal of NH₃

NH₃ is injected as an effective additive in the removal of SO₂ and NOₓ. At the same time, NH₃ is not acceptable because it produces a new environmental problem. To clarify the function of NH₃ in this process, the experiments of the removal of NH₃ are conducted in the flue gases with different conditions. The removal results are graphically presented in fig. 34. The figure shows that water content is the most important influence factor for NH₃ reduction. More than 85% of 900 ppm NH₃ can be removed even without any electrical energy input at 21% H₂O content while less than 40% of 720 ppm NH₃ is removed at 3% H₂O content in the case of up to 8 Wh/Nm³ energy input. As is well known, NH₃ is easily absorbed in water and, therefore, can be removed in the real flue gas. But removal of all NH₃ needs the electrical energy input, in particular, in the flue gas with low water content. In the flue gas with about 16% H₂O, which is used in majority of our experiments, about 50% of 900 ppm NH₃ can be removed as shown in fig. 34. With corona discharge, NH₃ can partly be dissociated by corona discharge into various radicals such as NH, NH₂ etc. These radicals convert NO to N₂. In the process of SO₂ and NOₓ removal, the formation of (NH₄)₂SO₄ and NH₄NO₃ through the chemical reactions play an important role for the reduction of NH₃ slip. These experimental results are in good agreement with [16].

![Figure 34: Removal of NH₃ in flue gases with different water.](image)

7. Discussion

- dc bias level

In the experiments on the dc bias effect on the removal of NO and NOₓ, it is found that the removal efficiency without dc bias is always better than that with dc bias. A use of dc bias being considered in general is to sweep the ions between two subsequent pulses in order to avoid the energy consumption on ions movement. At the first sight, the experimental results in fig. 15 seem to be contrary to this idea. But, in fact, a residual voltage exists on the discharge gap after a pulse. This residual voltage is probably enough to sweep ions in the gap. With an additional dc bias, the more energy is input into the gas. But the conduction current after the streamer crosses the gap is increased with the development of the secondary streamer. The waveshape analysis indicates that with a use of dc bias, the current pulse and corresponding the power pulse become 50 ns wider. From this point of view, the energy is not used effectively with a dc bias, in particular, when dc bias is over the corona onset value.

- Chemistry process

In general, the plasma chemical process in the removal of SO₂ and NO from flue gas by pulsed corona discharge consists of three steps as follow:
1) When positive streamers propagate from anode to cathode with a characteristic velocity of $10^5$-$10^6$ m/s, free electrons having a average energy of 10 eV are produced in the region of the front of the streamer head. Free electrons with such an energy can dissociate $\ce{O_2}$, $\ce{H_2O}$, $\ce{N_2}$ and $\ce{NH_3}$ to generate active radicals $\ce{O}$, $\ce{OH}$, $\ce{H}$, and $\ce{NH_2}$.

2) These active radicals initiate a large number of possible reactions to convert $\ce{SO_2}$ into $\ce{H_2SO_4}$ and $\ce{NO}$ into $\ce{HNO_3}$, $\ce{NO_2}$ and $\ce{N_2}$ through oxidation and reduction process. The ions and molecules produced by electrons also play an important role in the process. In this stage, the reaction is called homogeneous.

3) When ammonia is injected, the sulphate acid and nitric acid are converted to solid salts. At the same time, the heterogeneous phase reaction occurs at the surface of these particles. Also the autothermal reactions develop even without any external discharge energy input.

The streamer propagation, production of electrons and subsequent radicals, gas-phase chemical reactions have been extensively investigated by experiments and model calculations. The main chemical paths are simply summarized in fig.35.

![Fig. 35a: Reaction mechanism for removal of $\ce{SO_2}$](image)

![Fig. 35b: Reaction mechanism for removal of $\ce{NO}$](image)
-SO₂ removal

For removal SO₂ without any additive use, OH, mainly produced by direct dissociation of H₂O and hydrated ions, is suggested as the most important radical. The main removal reactions are:

SO₂ + OH → HSO₃
HSO₃ + O → SO₂ + HO₂
SO₃ + H₂O → H₂SO₄

The experimental results show that the removal of SO₂ by radical reaction is not very effective. Only less than 30 % of 300 ppm SO₂ is removed in the case of upto 10 Wh/Nm³ energy input. The similar results are also obtained by using barrier discharge [17] and electron-beam irradiation [18]. The removal of SO₂ ultimately depends on the number of OH radicals produced which in turn depends to a first order on power deposition. When NH₃ is injected, the removal of SO₂ is remarkably enhanced. In this case, the thermal reaction of SO₂-NH₃ leads to radical SO₂ removal. More energy input hardly improves the SO₂ conversion efficiency, but the slip NH₃ is significantly reduced. The by-product in this process is stable neutral sulphates (NH₄),SO₄ [3]. The thermal reaction of SO₂-NH₃ proceeds spontaneously and strongly depends on the gas temperature. By reducing the temperature, this thermal reaction is strengthened. But the by-products are acid sulphates rather than neutral sulphates and therefore leads to much higher NH₃. Acid sulphates can not be used as a fertiliser [3]. The apparent history effect in the removal of SO₂ with NH₃ injection is hard to explain with rapid gas-path reaction. The most likely explanation is the heterogeneous reaction because the aerosol formation and growth required longer time. The evidence of aerosol formation and enhancement on the removal of SO₂ is, however, still limited.

-Removal of NO and NO₃

The chemistry of the removal of NO and NO₃ is much more complex than the removal of SO₂ in the discharge plasma. At EUT, a set of 1000 chemical kinetics equations was solved using the KINEL program. The most important reactions for the gas-path process are found as [4-19].

NO+OH → HNO₂
NO+HO₂ → NO₂+OH
NO+N → N₂+O
NO₂+OH+M → HNO₃+M
NO+O → NO₂
NO+O→ O₂+NO₂
NO₂+O → NO+O₂
NO₂+H → NO+OH

The reduction and oxidation reactions are both involved in the process. Without NH₃ injection, the NO removal mainly follows the oxidation path. The reverse reaction of NO₂ with O or H is a main obstacle in the way of the conversion of NO to H₂NO₃. Even when NO₂ reacts with H₂O, a NO molecule forms [4].

3NO₂ +H₂O → 2HNO₃ +NO

So only two-thirds of the NO is eventually removed. The experimental result of a optimum residence time of 15 s is also evidence for this explanation. With NH₃ injection, there are two explanations for the
improvement of NO removal. The first is that the radicals NH₂ and NH produced by NH₃ dissociation react with NO: \[ \text{NO} + \text{NH}_2 \rightarrow \text{H}_2\text{O} + \text{N}_2 \]
\[ \text{NO} + \text{NH} \rightarrow \text{N}_2\text{O} + \text{OH} \]

The second is that HNO₃ is converted to NH₄NO₃. The general function of NH₃ can be thought that the formation of NO is inhibited by the presence of NH₃. With stoichiometric amount of NH₃, the high leak NH₃ indicates that the final products of NO conversion is not only NH₄NO₃.

The presence of 300 ppm SO₂ can improve NO conversion a factor three in the case of no NH₃ injection. This effect is also strong for NOX conversion. Though this fact is well known, the chemical mechanism is still unknown.

At EUT, the results of experiments and calculations have been put together. The calculated removal of NO molecules is still one to two order of amplitude lower than the value in reality. The most likely reason is that the heterogeneous reactions on the surface of aerosols and particles are not included in the model calculations.

- Combined removal of SO₂ and NO

The importance of the heterogeneous reactions has been emphasized by the present experiments on combined removal of SO₂ and NO. As indicated in fig.31, a time-dependence of the removal of NO with NH₃ injection is observed with a good reproducibility. The general tendency of the variation of NO concentration is quite similar to the variation of particle number as obtained in [18]. Concerning the strong synergetic effect between SO₂, NO and NH₃ on the removal of NO, the adjustment of the location of or NH₃ injection on the discharge reactor can enlarge this effect. The best results, i.e., 95 % and 85 % NO removal with 3 ppm leak NH₃ at 4 Wh/Nm² (13 eV/NO), are obtained under the considerations in several aspects:

1) The gas temperature is set at about 80 °C with 16% H₂O in the flue gas. The liquid-path reaction is possible to occur after the gas passed through the discharge reactor.

2) The optimum gas residence time of 15 s is used for this discharge reactor.

3) DC bias level is lower than its corona onset value.

4) SO₂ and NH₃ are injected at the different location of the reactor. The positive effect on the NO removal is effectively used.

5) Since the width of voltage and current pulses used in the experiments are three times larger than the streamer transit time of 30-40 ns, it could expected that the removal efficiency is further improved with shorter pulses.

- Two-stage treatment

The attempt to conduct two-stage treatment experiments is encouraged by the existing experiments with electron-beam irradiation. In the electron-beam irradiation treatment, the higher NOX removal efficiency could be achieved in the double- and triple-stage irradiation compared to single-stage irradiation. The enhancement effect of the multi-stage irradiation is thought due to the conversion of some intermediate products such as nitrous acid (HNO₂) to stable forms during the irradiation pause in
between the multi-stage irradiation, the intermediate products will be decomposed through the reaction with OH radical to produce NO, during the continuous irradiation [13]. This improvement does not appear in our experiments with pulsed corona discharge. This difference is probably ascribed to the difference between the two processes of the distribution of the electrons both in energy and space. In a streamer corona electrons are produced in thin discharge channels with an average energy of about 10 eV while in electron-beam irradiated gas the spatial distribution of electrons, with an energy of the order of 100 eV [20], is rather uniform. In a wire-cylinder discharge geometry the streamers fill only a small fraction of volume, i.e., 10^{-3}-10^{-4} [4]. The majority of the volume in the electrode gap is streamer free while a pulse is applied on the gap. On the other hand, the pulsed corona discharge is a process with a sequence of pauses. Therefore is not necessary to interrupt the discharge. In other words, in the pulsed corona discharge process, the double-stage treatment can not improve the cleaning efficiency.

8. Conclusions

1. UV absorption to simultaneously detect NO (0-450 ppm), SO₂ (0-1000 ppm) and NH₃ (0-1000 ppm) is applied to the flue gas cleaning process with pulsed corona discharge. The measurement error is in all cases below 5% despite of spectral overlap. The good agreement on the removal effects with results from literature shows that this is a viable method.

2. DC bias increases the power input into the gas. But the cleaning efficiency for NO and NOₓ becomes lower. This effect is stronger when the bias is above corona onset. The possible reason is that the pulses of current and power become wider and therefore the energy is not used effectively.

3. Considering the removal efficiency of NOₓ and SO₂, the stability of by-products and the property of pulsed corona, optimum temperature is that just over water condensation;

4. The NO and NOₓ removal requires the lowest power input at a residence time of about 15 s in this system. An optimum residence time for removal of NO/NOₓ can be explained using reverse reactions. In the presence of SO₂ and NH₃, the reverse reactions of conversion of NO are likely to be inhibited, there is probably not such an optimum residence time.

5. The auto-thermal reaction of SO₂-NH₃ is dominant for SO₂ removal, but the slip NH₃ is high and the by-products are acid sulfite. The increase in input of discharge energy has only a small influence on the SO₂ removal, but the slip of NH₃ can be reduced to almost zero by increasing the power input. In combination of corona discharge and NH₃ injection, the by-products are sulfates which can be directly used as a fertilizer.

6. With corona discharges and NH₃ injection, it is found that the removal rates of SO₂ depend on the history of energizating the discharge, but hardly depend on the energy input. This history effect can improve the SO₂ removal rate by 20%. In this process, NH₃ slip always depends on the energy input. This effect has not been explained well but it is supposed to relate to the formation of aerosols and/or salts.
7. \( \text{NH}_3 \) injection enhances the NO removal but its slip is high. The effect of \( \text{NH}_3 \) injection on the NO removal is thought to be due to the reduction of the formation of NO through the increase in the reduction reaction and nitric salts. The chemical mechanism in NO removal with \( \text{NH}_3 \) injection has, up to now, been unknown. Further investigations to explain high slip of \( \text{NH}_3 \) and low salts formation are needed.

8. 300 ppm \( \text{SO}_2 \) or 600 ppm \( \text{NH}_3 \) presence can enhance NO removal a factor three or two in 70 °C flue gas with 6 s residence time. However, in combination, the enhancement becomes less than either of them. The knowledge to explain this phenomenon can be a topic for the further study.

9. Synergetic effects on NO removal can be enlarged through adjusting locations of \( \text{SO}_2 \) or \( \text{NH}_3 \) injection. When 1200 ppm \( \text{NH}_3 \) is injected later, 81 % removal of 320 ppm NO (23 eV/NO) and over 98 % removal of 600 ppm \( \text{SO}_2 \) with less than 5 ppm leak \( \text{NH}_3 \) have been obtained at 7 Wh/Nm³. In the case of 900 ppm \( \text{NH}_3 \) injection before the reactor and 300 ppm \( \text{SO}_2 \) injection later, 81 % removal of 320 ppm NO(25 eV/NO) and 97 % \( \text{SO}_2 \) removal are achieved with about 2 ppm \( \text{NH}_3 \) slip at 7.5 Wh/Nm³. For the real flue gas, only the location adjustment for \( \text{NH}_3 \) injection is of practical importance.

10. The experiments on the removal of NO/NOₓ and simultaneous removal of NO and \( \text{SO}_2 \) show that no improvement is given by using two-stage treatment instead of one-stage treatment. The results are quite different from the results obtained with electron-beam irradiation. This difference is probably ascribed to the difference of spatial and energy distribution of electrons between the two processes.

11. The best results, i.e. 95 % \( \text{SO}_2 \) and 85 % NO (about 13 eV/NO) removal with 3 ppm leak \( \text{NH}_3 \), are obtained at the conditions of 80 °C, 15 s residence time and 15 kV dc bias with synergetic and history effects.

12. With shorter pulses and no dc bias, 50 % improvement of NO removal efficiency is still expected. A suggestion for the further measurements is to evaluate the maximum cleaning efficiency using the conditions close to full optimization (temp.: around 70 °C, residence time: about 15 s, half-width of current pulses: 20-30 ns, dc bias: 0 kV, \( \text{NH}_3 \) injection: at half way of reactor, NO measurement: waiting for a stable concentration at the exit of system).
9 References


Plasma-induced catalysis: a feasibility study and fundamentals.

Preliminary pilot plant tests of a corona discharge-electron beam hybrid combustion flue gas cleaning system.

Removal of SO₂ by pulsed corona streamer.

Modelling of the removal of nitric monoxide from exhausts by dielectric barrier discharges.

Application of E-beam treatment to flue gas cleaning in Japan.

Gas cleaning with semi-wet type plasma reactor.

Removal of SO₂ and the simultaneous removal of SO₂ and NO from simulated flue gas streamers using the dielectric barrier discharge plasmas.

[18] Frank, N.W. and S. Hirano
The history of electron beam processing for enviromental pollution control and work performed in the United States.

[19] Christensen, P.S.
The formation of areosols from SO₂ and NH₃ in humid air.

[20] Creyghton, Y.L.M.
Pulsed positive corona discharges: fundamental study and application to flue gas treatment.
Faculty of Electrical Engineering

(277) Weiland, Siep

(278) Gorshkov, Yu.A. and V.I. Vladimirov

(279) Creyghton, Y.L.M. and W.R. Rutgers, E.M. van Weelhuizen
In-Situ Investigation of Pulsed Corona Discharge.

(280) Li, H.Q. and R.P.P. Smeets
Gap-Length Dependent Phenomena of High-Frequency Vacuum Arcs.

(281) Dr. Chennia and Jochen A.G. Jess
On the Development of a Fast and Accurate Bridging Fault Simulator.

(282) Falkus, H.M. and A.A.H. Damen

(283) Meng, Y.Z. and J.G.J. Sloot
Thermal Buckling Behaviour of Fuse Wires.

(284) Rangelrooij, A. van and J.P.M. Voeten
CCSTool2: An expansion, minimization, and verification tool for finite state CCS descriptions.

(285) Roer, Th.G. van de
Modeling of Double Barrier Resonant Tunneling Diodes: D.C. and Noise Model.

(286) Dolmans, G.
Electromagnetic Fields Inside a Large Room with Perfectly Conducting Walls.

(287) Liu, Boshu and P. Messee
Reliability Analysis of Auxiliary Electrical Systems and Generating Units.

(288) Weiland, Siep and Anton A. Stoorvogel
Optimal Hankel Norm Identification of Dynamical Systems.

(289) Konieczny, Pawel A. and Lech Jozwiak
Minimal Input Support Problem and Algorithms to Solve It.

(290) Voeten, J.P.M.
PooSL: An object-oriented specification language for the analysis and design of hardware/software systems.
Ceden: TEUEDE
Faculty of Electrical Engineering

(291) Smeets, B.H.T. and M.H.J. Bollen
STOCHASTIC MODELLING OF PROTECTION SYSTEMS: Comparison of four mathematical techniques.

(292) Voeten, J.P.M. and A. van Rangelrooi

(293) Voeten, J.P.M.
SEMANTICS OF POOLS: An object-oriented specification language for the analysis and design of hardware/software systems.

(294) Osch, A.W.H. van
MODELLING OF PRASEODYMIUM-DOPED FLUORIDE AND SULFIDE FIBRE AMPLIFIERS FOR THE 1.3 µM WAVELENGTH REGION.

(295) Bastiaans, Martin J.

(296) Blaschke, F. and A.J.A. Vandenput
REGELTECHNIEKEN VOOR DRAAIVELDMACHINES. (Control of AC machines, in Dutch)

(297) Dolmans, G.
DIVERSITY SYSTEMS FOR MOBILE COMMUNICATION IN A LARGE ROOM.

(298) Maziz, J. and J.L.F. Balseiro
MODELLING OF A FLUIDIZED BED REACTOR FOR ETHYLENE POLYMERIZATION.

(299) Buterweck, H.J.
ITERATIVE ANALYSIS OF THE STEADY-STATE WEIGHT FLUCTUATIONS IN LMS-TYPE ADAPTIVE FILTERS.

(300) Horck, P.E.M. and L.J.P. van der Meeren, P.C.T. van der Leeg
COUPLING ON A MULTILAYER PRINTED CIRCUIT BOARD AND THE CURRENT DISTRIBUTION IN THE GROUND PLANE.

(301) Veen, J.L.F. van der and L.J.J. Offringa
ROTOR LOSSES IN A HIGH SPEED SYNCHRONOUS GENERATOR WITH PERMANENT MAGNET EXCITATION AND RECTIFIER LOAD.

(302) Zhou, L.M. and E.M. van Veldhuizen
MEDIUM-SCALE EXPERIMENTS ON NO/NO2 FROM FLUE GAS BY PULSED CORONA DISCHARGE.