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TECHNICAL REPORT
March 1 through May 31, 1995

Project Title: **COMBINED REMOVAL OF SO_x AND NO_x FROM FLUE GAS
USING NON-THERMAL PLASMA**

DOE Cooperative Agreement Number:	DE-FC22-92PC92521 (Year 3)
ICCI Project Number:	94-1/2.1A-4P
Principal Investigator:	Shirshak K. Dhali, SIUC
Project Manager:	Frank I. Honea, ICCI

ABSTRACT

A model has been developed to predict the performance of a dielectric-barrier discharge for various parameters. The model calculations have been compared with experimental results and are in close agreement for both SO₂/NO removal. The reaction scheme shows that OH is the most important radical for SO₂ removal with the final product being H₂SO₄. Whereas for NO removal both oxidation by OH to form HNO₃ and reduction by N to form N₂ are important channels.

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EXECUTIVE SUMMARY

The primary objective of the proposed research is to investigate a novel scheme for the simultaneous removal of SO_2/NO_x using a non-thermal plasma technique (dielectric-barrier corona discharge). Since the proposed approach also has the potential to remove volatile organic compounds (VOC) and hazardous trace elements, a study will be done on the removal of elemental mercury.

A model has been developed to predict the performance of a dielectric-barrier discharge for various parameters. The model calculations have been compared with experimental results and are in close agreement. These results have been submitted for publication to the Journal of Applied Physics.

Figure 1 shows the removal of SO_2 as function of energy densities. The solid circles in the figure are experimental data, which were obtained from a coaxial geometry dielectric-barrier discharge with an inner electrode of 3.0 mm in diameter,

an outer electrode of 2.3 cm, a glass dielectric of 1.5 mm thickness and 5.0 cm length of electrode. The SO_2 concentration in the gas mixture was 670 ppm (part per million) and the flow rate was 6000 SCCM (standard cubic centimeter per minute). The power supply frequency was 500 Hz and the power deposited to the discharge was controlled by the applied voltage. The solid line was obtained from the simulation of the experiment and with the temperature of the gas at 400 K. The dotted line was obtained at the same simulation condition of the solid line except that the temperature of the gas was allowed to increase linearly with the energy density.

The experimental results show that the removal efficiency increases with increasing energy density. However, it eventually saturates at higher energy densities. In the simulation, the critical reduced field is used for all calculations although the applied voltage may be different, because the global electric field is around the critical field as the result of the balance between ionization and attachment processes. The two simulation results also show an increase in removal efficiency with increasing energy density. But if

the simulated gas temperature is fixed at 400 K, the removal efficiency does not saturate as it did in the experimental results. The saturation can be explained if there is a gas temperature increase at higher energies. The dotted line shows the simulation results with a temperature increase as a function of energy density given by:

$$T = 400 + 2 \times (\langle e \rangle - 100) \times 1.8 / 2.3$$

Here $\langle e \rangle$ is the energy density and the unit is mJ/cc. This relation was found by trial-and-error.

The major end product of the removal of SO_2 is H_2SO_4 . The evolution of SO_2 and H_2SO_4 in the discharge for the initial gas mixture of 80% N_2 , 6% O_2 , 5% H_2O and 9% CO_2 at 400K and concentration of SO_2 of 670 ppm is given in Figure 2. The discharge is pulsed at 500 Hz with an energy density of 200 mJ/cc. The reaction product accumulates with each pulse in the gas stream. For these conditions, about 65% of SO_2 is converted into H_2SO_4 .

Fig. 2. The time evolution of SO_2 and H_2SO_4 in the discharge. The energy density is fixed at 200 mJ/cc. Other conditions are same as Fig. 1.

OBJECTIVES

The primary objective of the proposed research is to investigate a novel scheme for the simultaneous removal of SO_2/NO_x using a non-thermal plasma technique (dielectric-barrier corona discharge). Since the proposed approach also has the potential to remove volatile organic compounds (VOC) and hazardous trace elements, a study will be done on the removal of elemental mercury. Specifically, the following will be done to accomplish the above stated objectives.

1. *Optimization of the discharge for the removal of SO_2 and NO_x without additives:*
2. *Study the reduction of NO_x with ammonia injection in to the plasma:*
3. *Study of the removal of mercury and volatile organic compounds (VOC):*

INTRODUCTION AND BACKGROUND

In a plasma, chemical reactions can take place which is ordinarily not possible without a catalyst. We have conclusively demonstrated that plasma chemistry alone is sufficient to convert SO_2 to H_2SO_4 , the plasma being produced by a dielectric-barrier discharge. We get nearly 80% removal of SO_2 in a flue gas containing 775 ppm (parts per million) of SO_2 and 99% for SO_2 in concentrations of 300 ppm. However many questions have to be answered before this technique can be put to practical use.

Theory and experiments suggest that chemical reactions in the plasma are favorable for the removal of SO_2/NO_x . In a dielectric-barrier discharge, the dissociation of water and oxygen by electrons produce hydroxyl radicals and oxygen atoms, and the reactions are shown below,

The O and OH radicals react with SO_2 to form H_2SO_4 , and the reaction scheme is shown below;

The H_2SO_4 forms droplets which can be removed from the gas stream by an electrostatic precipitator.

For the removal of NO, the following reaction scheme is proposed

The HNO_3 produced as an end product of the reaction may be removed by injection of NH_3 or $\text{Ca}(\text{OH})_2$ to form NH_4NO_3 or $\text{Ca}(\text{NO}_3)_2$ respectively. The particles thus formed can then be removed from the gas stream by an electrostatic precipitator.

The proposed reaction scheme is the same as the Thermal DeNO_x process (Lyon 1987) which takes place in the temperature range of 900-1100 °C. However in a plasma the reactions are possible at temperatures below 300 °C and these reactions are shown below;

This study will be done for a set of parameters that are typical for coal-fired combustion facility.

The list of chemical substances that must be monitored and controlled under evolving environmental regulations is increasing rapidly. The Clean Air Act Amendments list 190 chemicals, many of which are emitted by fossil fuel-fired boilers. These guidelines will provide the technical basis for selecting appropriate control technology options to meet both current and proposed environmental regulations. Coal contain various mercury compounds, probably bound to sulfur in one way or another. It is very likely that during combustion process (above 700 °C), the compounds are thermally decomposed giving elemental mercury. It is also likely that divalent Hg is reduced on the surface of a burning particle. When the combustion gases are cooled, a small fraction of the mercury is oxidized. Oxidized mercury has its advantages and disadvantages: the disadvantage is that, HgO is more hazardous to the local environment if released to the atmosphere; the advantage is that it is easier to retain in flue gas cleaning system. For power plants with efficient collection systems, it is an advantage to convert elemental mercury to its oxide. In a dielectric-barrier discharge, oxygen atoms are readily created by electron-impact dissociation and the oxidation reaction below 600 °C can be achieved.

RESULTS AND DISCUSSIONS

All the experimental results reported in this section were performed at atmospheric pressures (760 Torr) and inlet gas was at room temperature. The basic composition of the gas consisted of a mixture of 80% N_2 , 6% O_2 , 5% H_2O and 9% CO_2 . The SO_2 concentrations with the discharge turned off and the discharge turned on were measured to obtain the percent η (%) removal from the flue gas stream:

$$\eta(\%) = \frac{([\text{SO}_2]_{\text{off}} - [\text{SO}_2]_{\text{on}})}{[\text{SO}_2]_{\text{off}}} \times 100$$

Figure 1 shows the removal of SO₂ as function of energy densities. The solid circles in the figure are experimental data, which were obtained from a coaxial geometry dielectric-barrier discharge with an inner electrode of 3.0 mm in diameter, an outer electrode of 2.3 cm, a glass dielectric of 1.5 mm thickness and 5.0 cm length of electrode. The SO₂ concentration in the gas mixture was 670 ppm (part per million) and the flow rate was 6000 SCCM (standard cubic centimeter per minute). The power supply frequency was 500 Hz and the power deposited to the discharge was controlled by the applied voltage. The solid line was obtained from the simulation of the experiment and with the temperature of the gas at 400 K. The dotted line was obtained at the same simulation condition of the solid line except that the temperature of the gas was allowed to increase linearly with the energy density.

The experimental results show that the removal efficiency increases with increasing energy density. However, it eventually saturates at higher energy densities. In the simulation, the critical reduced field is used for all calculations although the applied voltage may be different, because the global electric field is around the critical field as the result of the balance between ionization and attachment processes. The two simulation results also show an increase in removal efficiency with increasing energy density. But if the simulated gas temperature is fixed at 400 K, the removal efficiency does not saturate as it did in the experimental results. The saturation can be explained if there is a gas temperature increase at higher energies. The dotted line shows the simulation results with a temperature increase as a function of energy density given by:

$$T = 400 + 2 \times (\langle e \rangle - 100) \times 1.8 / 2.3$$

Here $\langle e \rangle$ is the energy density and the unit is mJ/cc. This relation was found by trial-and-error.

The major end product of the removal of SO₂ is H₂SO₄. The evolution of SO₂ and H₂SO₄ in the discharge for the initial gas mixture of 80% N₂, 6% O₂, 5% H₂O and 9% CO₂ at 400K and concentration of SO₂ of 670 ppm is given in Figure 2. The discharge

is pulsed at 500 Hz with an energy density of 200 mJ/cc. The reaction product accumulates with each pulse in the gas stream. For these conditions, about 65% of SO₂ is converted into H₂SO₄.

Fig 3. The removal of SO₂ as a function of concentration. Conditions are same as Fig. 2.

Figure 3 shows the removal of SO₂ as a function of concentration. Here the solid circles are experimental data and the solid line is obtained from the simulation. The conditions used for the simulation are the same as

Fig. 4. The removal of NO as a function of energy density.

hyperbolic nature of the curve indicates that at a fixed energy deposition, the percentage removal and concentration of SO_2 is fixed for higher SO_2 concentrations.

All the experimental results reported in this section were performed at atmospheric pressures (760 Torr) and inlet gas was at room temperature. The basic composition of the gas consisted of a mixture of 80% N_2 , 9% O_2 , 2% H_2O and 9% CO_2 . The NO concentrations with the discharge turned off and the discharge turned on were measured to obtain the percent η (%) removal from the flue gas stream:

$$\eta(\%) = \frac{([\text{NO}]_{\text{off}} - [\text{NO}]_{\text{on}})}{[\text{NO}]_{\text{off}}} \times 100$$

Figure 4 shows the removal of NO as a function of energy densities. The line with solid circles in the Figure are experimental data, which were obtained from a coaxial geometry dielectric-barrier discharge with an inner electrode of 3.0 mm in diameter, an outer electrode of 1.8 cm, a glass dielectric of 1.5 mm thickness and 5.0 cm length of electrode. The concentration of NO in the gas mixture was 320 ppm and the flow rate was 6000 SCCM. The power supply frequency was 500 Hz and the power deposited to the discharge was controlled by the applied voltage. The line with solid boxes was obtained by the simulation of the experiment and with a temperature of the gas at 400K. The line with solid triangles was obtained at the same simulation condition of the line with boxes except that the temperature increases as a function of the energy density:

$$T = 400 + 2 \times (\langle e \rangle - 30)$$

Here $\langle e \rangle$ is the energy density and the unit is mJ/cc.

The experimental data show that the removal efficiency increases in the low energy density range with an energy density increase and peaks at an energy density of about 58 mJ/cc, then it decreases as the energy density increases. It is likely that there is a gas temperature increase during the discharge and the temperature significantly effected the removal of NO. Because some of the energy was used to heat the gas, the experimental data are lower than the simulation data. From the simulation we can see that if the gas temperature remains constant, the percentage removal increases with increasing energy

those of Figure 1, except here the energy density (200 mJ/cc) and temperature of the gas (400 K) are fixed.

Clearly at low concentrations of SO_2 nearly complete removal can be achieved. For a higher concentration of SO_2 (2000 ppm), the radicals required for removal are not sufficient for complete removal and only 30% of the SO_2 is removed. The

temperature remains constant, the percentage removal increases with increasing energy deposition. However, if the gas temperature increases as the energy density increases, the removal efficiency shows a decrease with an energy density increase. The reason that the efficiency decreases with a temperature increase is that many reaction rates for this process are temperature dependent, and the total effect results in a decrease of the removal.

The major end products of the remediation of NO are N_2 , NO_2 , N_2O , N_2O_5 , HNO_2 and HNO_3 . The predicted removal of NO and generation of major end products for

Fig. 5. The time evolution of NO, N_xO_y , N_2 and HNO_3 in the discharge. The energy is fixed at 100 mJ/cc.

initial gas mixture of 80% N_2 , 9% O_2 , 2% H_2O and 9% CO_2 at 400K and a concentration of NO of 320 ppm is shown in Figure 5. The discharge was pulsed at 500 Hz with an energy deposition of 100 mJ/cc. The densities of the reaction products HNO_2 and HNO_3 , the incremental change in density of N_2 [$N_2 = N_2(t) - N_2(t=0)$], and the restricted N_xO_y product (NO_2 , N_2O , N_2O_5) generally

incrementally increase with each pulse as the products accumulate in the gas stream. An exception is the reaction product of NO_2 which itself reacts with plasma generated radicals and is ultimately removed. The result is that N_xO_y increases with time in the beginning of the process and then decreases with time. For these conditions, about 33% of NO is converted to N_2 through the reduction channel and approximately 28% is converted to HNO_3 through the oxidation channel. Small amount of the restricted oxides of nitrogen are formed. By investigating the pathway which dominated the removal of NO, we found that the percentage removal through the reduction channel increases as the energy density increases.

Disclaimer Statement

"This report was prepared by S. K. Dhali, Southern Illinois University with support, in part by grants made possible by the U. S. Department of Energy Cooperative Agreement Number DE-FC22-92PC92521 and the Illinois Department of Energy through the Illinois Coal Development Board and the Illinois Clean Coal Institute. Neither S. K. Dhali, Southern Illinois University nor any of its subcontractors nor the U. S. Department of Energy, Illinois Department of Energy & Natural Resources, Illinois Clean Coal Institute, nor any person acting on behalf of either:

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PROJECT MANAGEMENT REPORT

March 1 through May 31, 1995

**Project Title: COMBINED REMOVAL OF SO_x AND NO_x FROM FLUE GAS
USING NON-THERMAL PLASMA**

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 3)

ICCI Project Number: 94-1/2.1A-4P

Principal Investigator: Shirshak K. Dhali, SIUC

Project Manager: Frank I. Honea, ICCI

COMMENTS

None

PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Cost	Total
Sept. 1, 1994 to Nov. 30, 1994	Projected	4,937	0	1,250	0	0	1,250	744	8,181
	Estimated	4,937	0	1,000	0	0	1,000	694	7,631
Sept. 1, 1994 to Feb. 28, 1995	Projected	9,874	0	2,500	700	0	2,500	1,557	17,131
	Estimated	9,874	0	2,000	700	0	2,500	1,507	16,581
Sept. 1, 1994 to May 31, 1995	Projected	14,811	0	3,750	1,400	0	3,750	2,371	26,082
	Estimated	14,811	500	3,750	700	0	3,000	2,276	25,037
Sept. 1, 1994 to Aug. 31, 1995	Projected	38,583	3,409	5,000	2,000	0	5,000	5,399	59,391
	Estimated								

*Cumulative by Quarter

CUMULATIVE COSTS BY QUARTER

Combined Removal of SO_x and NO_x from Flue Gas Using Non-Thermal Plasma

● = Projected Expenditures -----
▲ = Actual Expenditures _____

Total Illinois Clean Coal Institute Award \$59,391

SCHEDULE OF PROJECT MILESTONES

Begin
Sept. 1
1994

Hypothetical Milestones:

- A: Optimization of discharge parameters
- B: No_x removal with NH_3 injection
- C: Mercury Removal
- D: Technical and Project Management Reports