DOE/PC/92521--T250

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TECHNICAL REPORT
December 1, 1994 through February 28, 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

The removal of NO_X from flue gas was studied during this period. About 44% of NO_X in concentrations of about 400 ppm and 100% of NO_X in concentrations below 80 ppm can be removed without any chemical additives. Also some preliminary experiments have been done on the combined removal of SO_2 and NO. Indications are that the NO in the flue gas helps the removal of SO_2. Work is continuing on the combined removal at present.

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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.

The removal of NO_X from flue gas was studied during this period. About 44% of NO_X in concentrations of about 400 ppm and 100% of NO_X in concentrations below 80 ppm can be removed without any chemical additives. For these experiments no chemical additives were added to the discharge.

A convenient parameter used to describe the power input to the discharge is the average energy density which is defined as the (average power input)/(flow rate of the gas). This quantity gives a measure of the amount of electrical energy inputted per unit volume of the processed gas.

Shown in Fig. 1 is the typical removal efficiency of dielectric-barrier discharge reactor as a function of energy density. The two sets of data is for two different electrode lengths. As shown the energy density is critical in determining the removal percentage. Irrespective of the length of the electrode, the removal efficiency peaks at about 65-70 mJ/cc under the particular experimental condition. The decrease in the removal efficiency with higher energy density can be explained by the following reaction which produces NO:

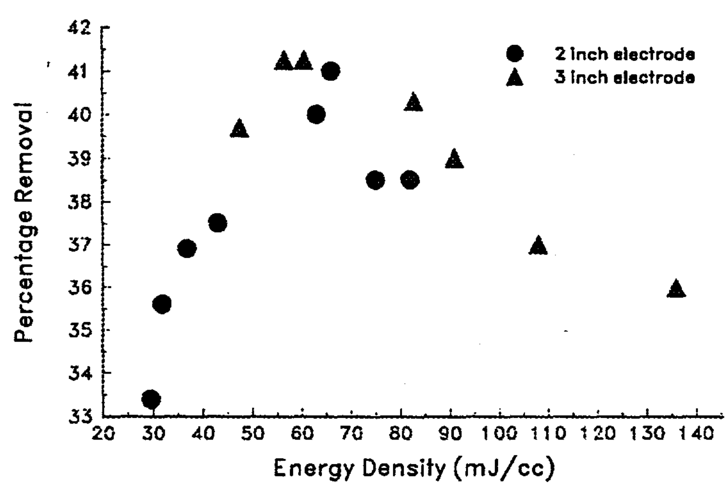

Fig. 1. Percentage removal of NO as a function of energy density. The $N_2/O_2/H_2O/CO_2$ is in the ratio of 75/5/2.6/15. The flow was at 6000 SCCM, pressure was 760 Torr and the temperature was at room 20°C.

$$NO_2 + O \rightarrow NO + O_2; 6.5\times10^{-12}\exp(120/T)$$

$$N + O + M \rightarrow NO + M; 5.46\times10^{-33}\exp(155/T)$$

Higher energy densities produce higher concentrations of N and O. As the concentration of NO_2 increases, the first reaction becomes dominant at high energies and any additional increase in energy does help in the removal of NO. Similarly, the second reaction produces more NO as the energy is increased again with a detrimental effect as shown in Fig. 1.

There is some indication that NO helps in the removal of SO_2. It is also likely that presence of SO_2 will help in the removal of NO. This is likely because SO_2 uses O radicals and thus impedes reaction shown above. The results of combined removal will be reported in the next quarterly report. Also the following additional experiments will be performed:

1. Study the combined removal with trace amounts of NH_3 (1000 ppm).
2. Study the effect of NO on the removal of SO_2 and vice versa.

Some of these results will be presented at a forthcoming workshop on the treatment of Gaseous Emissions via Plasma Technology. This workshop is being organized by National Institute of Standards and Technology at Gaithersburg, Maryland.

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,

$$O_2 + e \longrightarrow O + O(^1D) + e \xrightarrow{H_2O} OH + OH$$
$$H_2O + e \longrightarrow H + OH + e.$$

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

$$SO_2 + O \longrightarrow SO_3\ ; \qquad SO_3 + H_2O \longrightarrow H_2SO_4$$
$$SO_2 + OH \longrightarrow HSO_3; \qquad HSO_3 + OH \longrightarrow H_2SO_4$$

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

$$NO + O + M \longrightarrow NO_2 + M; \qquad NO_2 + OH \longrightarrow HNO_3.$$

The HNO_3 produced as an end product of the reaction may be removed by injection of NH_3 or $Ca(OH)_2$ to form NH_4NO_3 or $Ca(NO_3)_2$ 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 ^oC. However in a plasma the reactions are possible at temperatures below 300 ^oC and these reactions are shown below;

$$NH_3 + e \longrightarrow NH_2 + H + e \xrightarrow{NO} N_2 + H_2o$$
$$NH_3 \xrightarrow{OH} NH_2 \xrightarrow{NO} N_2 + H_2O$$
$$NH_3 \xrightarrow{O} NH_2 \xrightarrow{NO} N_2 + H_2O$$

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 ^oC), 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 ^oC can be achieved.

EXPERIMENTAL PROCEDURES

The experimental setup is shown in Fig. 2. The power supply for the discharge is a 2kW, 0 to 5 kHz ac source. The discharge electrode configuration currently in use is coaxial. The inner electrode is exposed metal (stainless steel) and the outer electrode is glass coated with a conducting surface.

The on-line diagnostics consists of emission spectroscopy, mass spectroscopy, and SO_2 pulsed fluorescence spectroscopy. The diagnostics are geared mainly towards estimating the species type and concentration. The main aim of the measurements is to understand the parameter influence on the removal of SO_2/NO_x. The main instrument available for SO_2 analysis is the Thermo-Electron Model 40 pulsed fluorescent SO_2 analyzer and for NO detection we have a Bacharach NONOXUR NO detector.

RESULTS AND DISCUSSIONS

For the results reported here, the dimension of the inner electrode (A) is 0.5 cm, and the inner diameter of the glass dielectric was fixed at 2 cm. The length of the outer electrode is 10 cm. All the experimental results reported were performed at atmospheric pressures (760 Torr) and inlet gas was at room temperature. The basic composition of the gas consist of $N_2/O_2/H_2O/CO_2$ in the ratio of 75/5/2.6/17. The NO concentration with discharge turned off and the discharge turned on were measured to obtain the percent $\eta(\%)$ removal from the flue gas stream:

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

During this reporting period, the removal of NO and combined removal of SO_2/NO from a simulated flue gas was studied. For these experiments no chemical additives were added to the discharge.

A convenient parameter used to describe the power input to the discharge is the average energy density which is defined as the (average power input)/(flow rate of the gas). This quantity gives a measure of the amount of electrical energy inputted per unit volume of the processed gas.

Shown in Fig. 1 is the typical removal efficiency of dielectric-barrier discharge reactor as a function of energy density. The two sets of data is for two different electrode lengths.

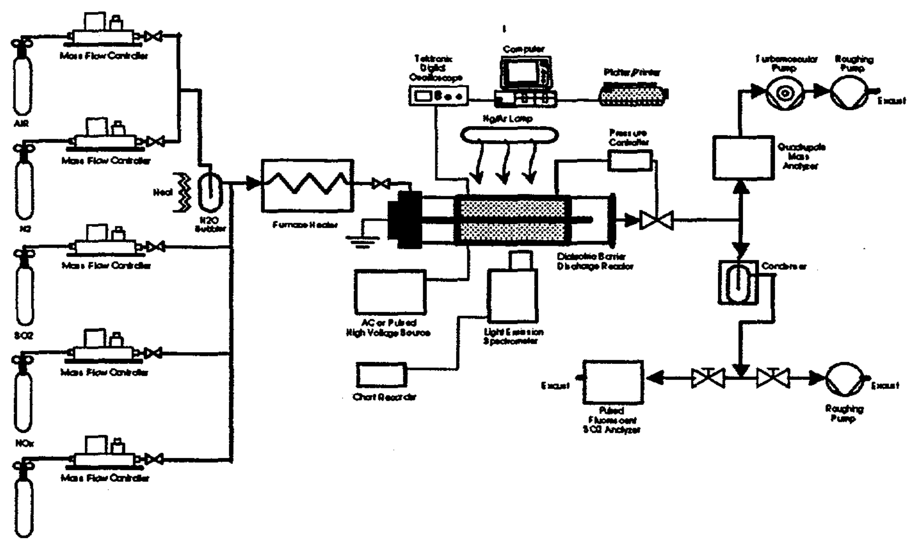

Fig. 2. The schematic of the experimental setup for the current project.

As shown the energy density is critical in determining the removal percentage. Irrespective of the length of the electrode, the removal efficiency peaks at about 65-70 mJ/cc under the particular experimental condition. The decrease in the removal efficiency with higher energy density can be explained by the following reaction which produces NO:

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A convenient parameter used to describe the power input to the discharge is the average energy density which is defined as the (average power input)/(flow rate of the gas). This quantity gives a measure of the amount of electrical energy inputted per unit volume of the processed gas. It is clear that increased removal of SO_2 at higher voltages comes at the expense of increased power input.

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
December 1, 1994 to February 28, 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, Department of Electrical Engineering, Southern Illinois University at Carbondale
Project Manager: Frank I. Honea, Illinois Clean Coal Institute

COMMENTS

None.

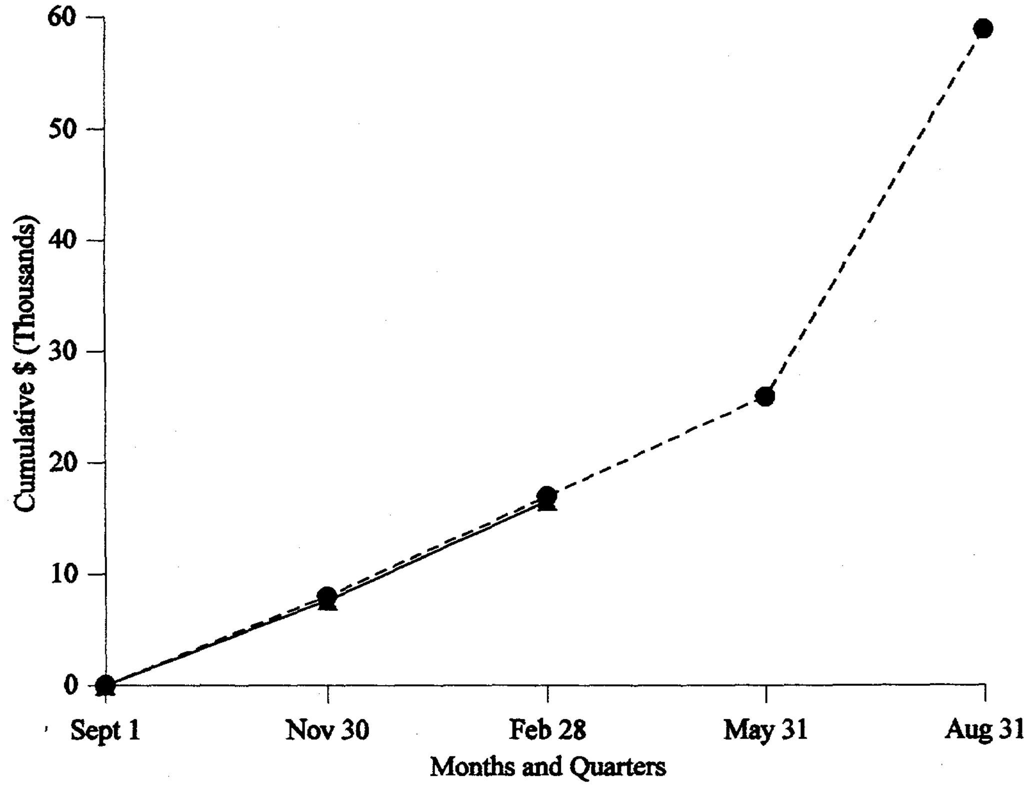
PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER

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								
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

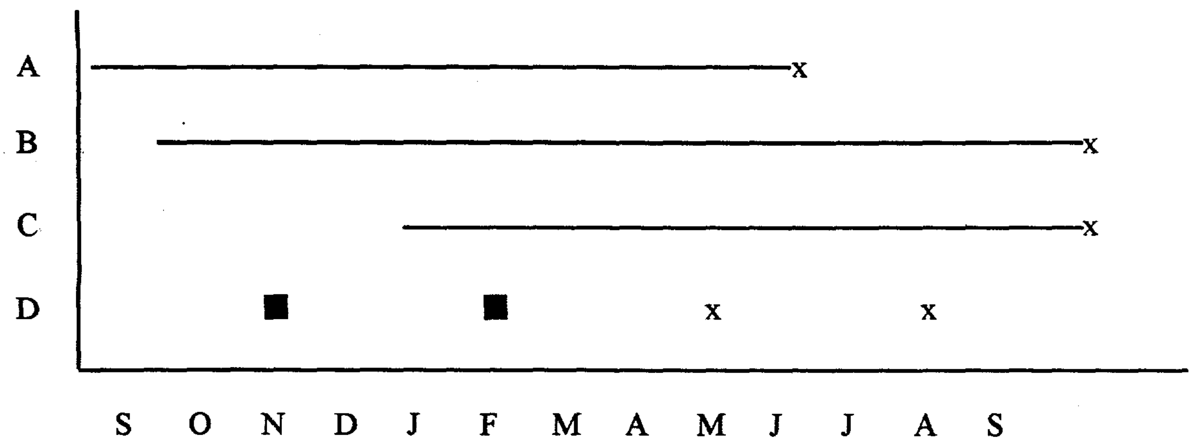
Combined Removal of So_x and No_x from Flue Gas Using Non-Thermal Plasma



● = Projected Expenditures - - - - - - -
▲ = Actual Expenditures ________

Total Illinois Clean Coal Instutute 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