TECHNICAL REPORT

September 1 through November 30, 1994

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 SO₂ removal efficiency was studied for concentration in the range of 333-3000 ppm (parts per million). Since the sulfur content of Illinois coal is high, the SO₂ concentration in typical flue gas is in the high end of the range shown above. With high concentration of SO₂ the removal efficiency decreases. However, the removal scales well with applied voltage, electrode length, and supply frequency.

In this period the modeling of the process was also accomplished. The results show that a Townsend-type discharge is more efficient than a streamer type discharge in producing OH and O radicals. This explains why UV-irradiation helps the removal efficiency. The details are discussed in the report.

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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.

Improvement in percent removal is not always accompanied by increased utilization of electrical energy. When a parameter is varied, the energy input also varies. The electrical energy utilization with relation to removal of SO_2 by a dielectric-barrier has not been reported in earlier papers because of the difficulty in measuring the energy associated with the random discharges. In order to obtain an estimate of the utilization of the electrical energy needs, the power input to the discharge has to be measured. For a dielectric-barrier discharge this can be done by measuring the discharge voltage and the charge transported through the discharge. The charge transported can be measured from the voltage across a large capacitor in series with 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. It is clear that increased removal of SO_2 at higher voltages comes at the expense of increased power input.

Shown in Fig. 1 is the typical removal efficiency of dielectric-barrier discharge reactor for different SO_2 concentration. Clearly at low concentrations of SO_2 efficient removal can be achieved. Although for high concentration of SO_2 (combustion of high sulfur coal produces 2500-3000 ppm) the removal is only 25-30%, the removal efficiency increases with increasing length of the electrode. With electrode length of 20 cm, the percent removal can be raised to about 60% for SO_2 concentration in the range of 2000 ppm. The increase in removal due to an increase in length is due to the increased residence time of the gas being processed.

Monte Carlo calculations of energy distributions, transport properties and dissociation coefficient rates of electrons in flue gas was done by tracking a single electron for 10^8 collisions. The flue gas consists of a mixture of individual gases whose electron impact cross section are available in the literature. The Monte Carlo calculation takes into account the detailed collisional processes in the gas to determine the electron energy distribution function (EEDF). Once the EEDF in particular gas at a given E/N (reduced field) is known, the rates can be determined from the cross section value.

The efficiency (G-factor) of $\text{O}(^3\text{P})$ and OH production are of the order of 1 per 100 eV of electrical energy input. Clearly the production of $[\text{O}]$ and $[\text{OH}]$ are not very energy efficient. Calculation for a flue gas with higher O_2 concentration shows a proportional increase in the G-factor.

In microdischarges, which are streamer type discharges, the expected G-factors will be lower than the Townsend type discharge. In order to get an estimate of G-factors in microdischarges, streamer calculations were performed in a flue gas. The transport and rate coefficients were obtained from the Monte Carlo calculation.

When electron avalanches develop to a critical size, the space charge field will make the field nonuniform and very high in certain regions. Photoelectrons generated ahead of the space-charge front causes a rapid growth in the high field and a fast propagation of the front. As can be expected the G-factors in a streamer discharge is about a factor of two lower compared to the Townsend type discharge.

These results were presented at the Non-thermal Plasma Session of the Emerging

Fig.1 Percentage SO₂ removal as a function of the energy density. The concentration of N₂/O₂/H₂O/CO₂ was in ratio of 75/5/2.6/17.4 with a total flow of 3000 SCCM at 760 Torr. The electrode length was 10 cm.

Technologies in Hazardous Waste Management VI Conference on September 19, 1994. This conference is sponsored by the Division of Industrial and Engineering Chemistry of the American Chemical Society.

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 (EPRI 1992). 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.

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 . A quadrupole residual gas analyzer with a pressure converter will be used to obtain the spectra of the effluent

Fig. 1. The schematic of the experimental setup for the current project.

from the reactor. This will be the main diagnostic tool for studying the NO_x removal process. The main instrument available for SO_2 analysis is the Thermo-Electron Model 40 pulsed fluorescent SO_2 analyzer.

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 $\text{N}_2/\text{O}_2/\text{H}_2\text{O}/\text{CO}_2$ in the ratio of 75/5/2.6/17. The SO_2 concentration with discharge turned off and the discharge turned on were measured to obtain the percent $\eta(\%)$ removal from the flue gas stream:

$$\eta(\%) = \frac{([\text{SO}_2]_{\text{off}} - [\text{SO}_2]_{\text{on}})}{[\text{SO}]_{\text{off}}} \times 100. \quad (1)$$

Improvement in percent removal is not always accompanied by increased utilization of electrical energy. When a parameter is varied, the energy input also varies. The electrical energy utilization with relation to removal of SO_2 by a dielectric-barrier has not been reported in earlier papers because of the difficulty in measuring the energy associated with the random discharges. In order to obtain an estimate of the utilization of the electrical energy needs, the power input to the discharge has to be measured. For a dielectric-barrier discharge this can be done by measuring the discharge voltage and the charge transported through the discharge. The charge transported can be measured from the voltage across a large capacitor in series with 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. It is clear that increased removal of SO_2 at higher voltages comes at the expense of increased power input.

Shown in Fig. 1 is the typical removal efficiency of dielectric-barrier discharge reactor for different SO_2 concentration. Clearly at low concentrations of SO_2 efficient removal can be achieved. Although for high concentration of SO_2 (combustion of high sulfur coal produces 2500-3000 ppm) the removal is only 25-30%, the removal efficiency increases with increasing length of the electrode. With electrode length of 20 cm, the percent removal be raised to about 60% for SO_2 concentration in the range of 2000 ppm. The increase in removal due to an increase in length is due to the increased residence time of the gas being processed.

MODEL CALCULATION OF RADICAL PRODUCTION

Monte Carlo calculations of energy distributions, transport properties and dissociation coefficient rates of electrons in flue gas was done by tracking a single electron for 10^8 collisions. The flue gas consist of a mixture of individual gases whose electron impact cross section are available in the literature. The Monte Carlo calculation takes into account the detailed collisional processes in the gas to determine the electron energy distribution function (EEDF). Once the EEDF in particular gas at a given E/N (reduced field) is known, the rates can be determined from the cross section value. The dissociation reactions listed below are of particular interest for pollution control treatment. These electron impact processes are the primary source of radicals required to remove the pollutants.

where k_i is the dissociation rate which can be obtained from the velocity distribution function $f(v)$ obtained from the Monte Carlo calculation [19]:

$$k_i = \int_0^{\infty} Q_i(v) f(v) v dv \quad (7)$$

where Q_i is the dissociation cross section of the collisional process, v is the electron velocity. The k_i is a function of the reduced field (E/N).

The radicals produced by electron impact undergo reactions with other radicals and molecules in the discharge. Shown below are the important reactions that determine the concentration of important radicals:

where M is the three body partner; k_i is the rate constant which is not dependent on E/N..

The waste destruction process is divided into three parts to simplify the calculations: (1) the discharge phase, (2) a post discharge phase where the excited radicals are quenched to form longer-lived radicals, and (3) a phase where the radicals react with the pollutants. The discharge phase is of the order of a few nanoseconds for streamer like microdischarges encountered in atmospheric pressure dielectric-barrier discharge. The order of quenching of excited radicals like $O(^1D)$ is of the order of few tens of nanoseconds or longer. The radical reaction with pollutants is of the order microsecond or longer.

For a generalized electron impact dissociation process, assume that a dissociated product with density [A] is produced from a parent gas with density [AB] with a rate constant k_A . If $\Delta\epsilon$ is the energy density in eV deposited into the discharge in time ΔT , then the radicals produced per 100 eV of energy due electron impact only is defined as,

$$Ge[A] = \frac{100 \times \Delta[A]}{\Delta\epsilon} \quad (13)$$

The overall efficiency of formation of radicals will involve the molecule-radical and radical-radical reactions listed earlier. The overall radical formation efficiency of the oxygen atom (O) and hydroxyl radical (OH) is given by

$$G[O(^3P)] = Ge[O(^3P)] + \frac{Ge[O(^1D)]}{1 + \frac{k_7[H_2O]}{k_6[O_2]}} \quad (14)$$

$$G[OH] = Ge[OH] + \frac{2 * Ge[O(^1D)]}{1 + \frac{k_6[O_2]}{k_7[H_2O]}} \quad (15)$$

For a Townsend like discharge, with a constant E/N (reduced field), the radical density $\Delta[A]$ at time ΔT is given by

$$\Delta[A] = k_A [AB] \int_0^{\Delta T} n_e dt. \quad (16)$$

The $\Delta\epsilon$, the energy density in eV deposited into the discharge in time ΔT , is given by

$$\Delta\epsilon = e^{-1} \int_0^{\Delta T} J E dt = v_d E \int_0^{\Delta T} n_e dt \quad (17)$$

where J the current density, E is the constant electric field, e is the unsigned electron charge, v_d is the drift velocity which is constant for a given E , and n_e is the electron density. For a Townsend type discharge

$$Ge[A] = 100 \frac{k_A \frac{[AB]}{N}}{v_d \left(\frac{E}{N} \right)} \quad (18)$$

where N is the total particle density. Therefore the overall G-factor (for a Townsend type discharge) for $O(^3P)$ and OH radicals may be expressed as

$$G[O(^3P)] = \frac{100}{v_d(E/N)} \left\{ (2k_1 + k_2) \frac{[O_2]}{N} + \frac{k_2 \frac{[O_2]}{N}}{1 + \frac{k_7[H_2O]}{k_6[O_2]}} \right\} \quad (19)$$

$$G[OH] = \frac{100}{v_d(E/N)} \left\{ k_4 \frac{[H_2O]}{N} + \frac{2k_2 \frac{[O_2]}{N}}{1 + \frac{k_6[H_2O]}{k_7[O_2]}} \right\} \quad (20)$$

The plot of the G-factor for OH and $O(^3P)$ radicals are shown in Fig. 3 for a flue gas with $N_2/O_2/H_2O/CO_2$ ratio of 80/6/5/9. The efficiency of $O(^3P)$ and OH production are of the order of 1 per 100 eV of electrical energy input. Clearly the production of $[O]$ and $[OH]$ are not very energy efficient. Calculation for a flue gas with higher O_2 concentration shows a proportional increase in the G-factor.

Fig. 3. The G-factor (radicals/100eV of electrical input) as a function of the applied electric field. This plot is for a Townsend type discharge.

In microdischarges, which are streamer type discharges, the expected G-factors will be lower than the Townsend type discharge. In order to get an estimate of G-factors in microdischarges, streamer calculations were performed in a flue gas. The transport and rate coefficients were obtained from the Monte Carlo calculation.

When electron avalanches develop to a critical size, the space charge field will make the field nonuniform and very high in certain regions. Photoelectrons generated ahead of the space-charge front causes a rapid growth in the high field and a fast propagation of the

Fig. 4. The G-factor (Radicals produced/100 eV of energy) for a streamer type discharge.

front. This effect of space charge dominated transport which occurs at high pressures (atmospheric) and high voltages is called the streamer mechanism. The simplest set of equation describing the streamer formation and propagation is the continuity equation for electrons, positive ions, and negative ions, coupled with the Poisson's equation for the electric field. The G-factors calculated for a streamer type discharge in a flue gas ($N_2/O_2/H_2O/CO_2$ ratio of 80/6/5/9) is shown in Fig. 4. As can be expected the G-factors in a streamer discharge is about a factor of two lower compared to the Townsend type discharge.

The third phase of the discharge involves the reaction of the radicals with the pollutants as described by the set of reactions given below. The O in these is the ground state oxygen atom $O(^3P)$.

where M is the third body whose concentration is the total gas density. Using the above rates, the radical utilization efficiency for the destruction of SO_2 is defined as [20]

$$\eta[O] = \frac{\partial[SO_2]}{\partial[O]} = \frac{k_{14}[SO_2][M]}{k_{14}[SO_2][M] + k_{15}[O_2][M] + k_{16}[O_3] + k_{13}[OH]} \quad (25)$$

$$\eta[OH] = \frac{\partial[SO_2]}{\partial[OH]} = \frac{k_{11}[SO_2]}{k_{11}[SO_2] + k_{12}[M] + k_{13} \frac{[O]}{[OH]}} \quad (26)$$

For $[SO_2] = 0.66 \times 10^{-3}[M]$ (667 ppm), $[O_2] = 6.0 \times 10^{-2}[M]$, and $[M] = 2.68 \times 10^{19} \text{ cm}^{-3}$, it $\eta[O] \approx 0.5$ and $\eta[OH] \approx 1$. Therefore, the total SO_2 removal efficiency (molecules removed per 100 eV of energy input is given by

$$\eta_t = G[O]\eta[O] + G[OH]\eta[OH]. \quad (27)$$

From Fig. 3 and Fig. 4 the maximum value of $\eta_t = 1.7$ and 0.5 for a Townsend and a streamer discharge respectively. For comparison with the experimental data, this can be

converted to kWh required per kg of SO₂ removed from the value η_t calculated above. For the Townsend and the streamer type discharge this number is 48 kWh and 166.8 kWh per kg of SO₂ removed respectively.

CONCLUSIONS

In conclusion, the data on electrical energy utilization is presented. The measured values of kWh required per kg of SO₂ removed is very close to the theoretical prediction. It is also apparent from the calculations that a Townsend type discharge is about three times more efficient in removing SO₂ compared to the streamer type discharge. Also the experimental results point to the fact the removal efficiency scales well with length of the chamber and power frequency.

Disclaimer Statement

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COMMENTS

None.