ABSTRACT

The objective of the proposed research is to design and implement a novel scheme for the combined removal of SO₂ and NOₓ using a dielectric-barrier discharge in conjunction with UV irradiation. This investigation requires the design of a dielectric-barrier reactor and testing the proposed scheme under different conditions that exist in a flue gas.

A reactor has been designed and electrical tests have been performed. The voltage characteristics of the plasma reactor has been studied. We have found that a discharge can be sustained at atmospheric pressures with a large inner electrode in the coaxial configuration.

The testing of the uniformity of the discharge with UV irradiation has been very successful. The details are provided in this report and has been submitted to the Applied Physics Letter. Also both experimental and simulation work were carried out on the removal of SO₂ and NOₓ. With the improved reactor, we have achieved a conversions of SO₂ up to 85%. The simulation studies indicate that complete removal of NOₓ is possible at reduced electric fields (E/N) of above 100 Td.

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EXECUTIVE SUMMARY

Under this investigation, a non-equilibrium plasma at atmospheric pressure is generated to process SO_2 and NO_x into products that are easy to remove. The plasma is generated by a dielectric-barrier discharge. Our past studies have indicated that the efficiency of removal of SO_x/NO_x is critically dependent on the uniformity of the dielectric-barrier discharge. A considerable amount of effort has been expended to improve the existing discharge.

The experimental results and simulations show that in a flue gas plasma, SO_2 is oxidized to SO_3 and simultaneously NO_x is reduced to N_2. The resulting SO_3 can be removed by a limestone spray dryer at large reduction in cost. This is the basic premises for the proposed research.

The first stage of the research consisted of the design and fabrication of the discharge chamber. The instruments for on-line diagnostics, which consist of emission spectroscopy, residual gas analysis, and SO_2 pulsed fluorescence spectroscopy, were put in place. The discharge parameters such as gas flow, gas pressure, gas composition are controlled by a set of mass flow controller and gate valves. This part of the system was tested and was found to perform to satisfaction. The schematic of the experimental setup along with discharge chamber is shown in Fig. 1.

![Diagram of experimental setup and discharge chamber](image)

Fig. 1. (a) Schematic of the experimental setup and (b) the details of the discharge chamber.

The critical electrical tests on the discharge chamber have been performed. A set of onset voltage versus pressure curves have been obtained for different electrode geometries. The results suggest that for a coaxial geometry a inner electrode with a larger radius needs lower onset voltage. Most of our experiments were done with the largest inner electrode possible.
We are able to achieve a stable and uniform discharge by UV irradiation of the dielectric-barrier. The number of microdischarges considerably increases with UV irradiations as shown in Fig. 2. The oscilloscope trace of the voltage and the current of Fig. 2a and 2b correspond to with and without UV irradiation. The intensity of the UV is approximately 10 μW/cm², which is a very low value.

The dielectric-barrier discharge is suitable for generating a non-thermal plasma for processing of flue and toxic gases. The use of very low levels of UV from a mercury lamp changes the discharge characteristics; the discharge is more uniform due the larger number of microdischarges.

The Fig. 3 shows the discharge voltage on Y-axis and the charge on X-axis. The area under the closed pattern is the energy input to the discharge per cycle. The product of the energy per cycle and the repetition rate gives the power input to the discharge. The oscilloscope traces were taken under the same conditions in all cases shown except for the presence or absence of UV. From Fig. 3 the energy deposited per cycle is 3 mJ and 2.1 mJ per cycle with and without UV. The discharge was operated at 1 KHz giving a average power of 3 and 2.1 W with and without UV respectively. The energy coupled to the discharge with UV is higher than without UV by approximately 50%. This energy goes into providing excited radicals such as O and OH atoms which are required for removal of SO₂ and NOₓ.
The increase in the energy coupling also increases the light emission from the discharge due to UV irradiation; the atomic oxygen emission line is enhanced. The efficiency of SO₂ removal is strongly dependent on the atomic oxygen production. There is an optimum pressure for a given coaxial geometry at which the emission of the oxygen line is maximum. We have very carefully investigated this dependence and this is shown in Fig. 4. The intensity of the line peaks at a certain pressure which is a function of the gap distance (in this the outer electrode and the dielectric are kept fixed and the inner electrode diameter is varied).

During the last quarter, the experimental investigation of the removal of SO₂ with the improved reactor was started. Shown in Fig. 5 is the fractional conversion of SO₂ as a function of the O₂ concentration. We were able to achieve up to 85% removal in dry air. The results shown in Fig. 5 may be off by about 10% due to the drifting of the photomultiplier in the SO₂ meter. Initial removal is proportional to the O₂ concentration. Further addition of O₂ increases the production of O₃, which is a competing process that uses up atomic oxygen.

The removal process is being studied with water vapor in the air and by varying other parameters. The setup for adding water to the system has been incorporated and a dew point hygrometer (Vaisala) is used to measure the humidity. The discharge is being studied with the water vapor present in the flue gas. The discharge is stable and uniform with about 6% H₂O in air. The

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**Fig. 4** The relative intensity of the oxygen atom line as a function of pressure. The parameter in the plot is the radius of the inner electrode. The outer electrode is kept fixed.

**Fig. 5** The fractional SO₂ removal. The experiments were done at atmospheric pressure and a flow rate of 2500 SCCM. Due to the drifting of the photomultiplier in the SO₂ meter, the percentage removal shown has an error of ±10%.
results on removal of SO2 water is too preliminary to be included in this report.

Simulation were carried out to understand the process of NOx removal by a dielectric-barrier discharge. The simulation studies were investigated in order to understand the conditions under which NOx removal is possible. Fig. 6 shows the fractional removal of NO as a function of E/N (reduced electric field). Clearly approximately 100 Td will be required to efficiently convert NO to atmospheric nitrogen. The different curves are for different concentration of NO in flue gas, and with higher concentration the field required is higher.

Testing on the improved discharge indicates that it operates at higher E/N's (reduced field). This is useful because the removal of NO requires high electric fields. The tests include electrical and optical emission spectroscopy for air, pure oxygen, pure nitrogen and, air with CO2 and SO2. These tests show that with an attaching gas (O2, CO2, and SO2) the discharge tends to form filamentary microdischarges. However, the use of UV irradiation tends to make the discharge more uniform. The results are encouraging because it shows that under most conditions a uniform atmospheric discharge can be maintained with UV irradiation.

The key to the use of a dielectric-barrier discharge is the maintenance of a uniform discharge under the adverse condition of a flue gas stream. We are able to achieve this through UV irradiation of the dielectric-barrier discharge.

The results of the study were presented at the EPRI Symposium on Environmental Applications of Advanced Oxidation Technologies. This symposium was jointly sponsored by EPRI and NSF. The PI visited the Los Alamos National Laboratory and presented a talk on the use of the dielectric-barrier discharge for pollution control. The group at Los Alamos is actively engaged in the use of non thermal plasmas for removal of VOC. This visit was mutually beneficial as it will result in the exchange of technical information.

Fig. 6 The fractional removal of NO as a function of the reduced electric field. The calculation were for flue gas at atmospheric pressure. The parameter is the concentration of NO in the flue gas.
OBJECTIVES

The objective of the proposed research is to design and implement a novel scheme for the combined removal of SO$_2$ and NO$_x$ using a dielectric-barrier discharge in conjunction with UV radiation. This investigation requires the design of a dielectric-barrier reactor and testing the proposed scheme under different conditions.

Specifically the following tasks were performed to accomplish the objectives:

1. Study the effect of UV-irradiation on the oxidation of SO$_2$ to SO$_3$ in a plasma.

2. Study the effects of discharge parameters on NO$_x$ removal.

3. Characterization of the flue gas.

4. Study (limited to data compilation) the possibility of removing volatile mercury in flue gas by plasma oxidation in a dielectric-barrier discharge.

INTRODUCTION AND BACKGROUND

Experimental results and simulations show that in a flue gas plasma, SO$_2$ is oxidized to SO$_3$ and simultaneously NO$_x$ is reduced to N$_2$. The resulting SO$_3$ can be removed by a limestone spray dryer at large reduction in cost. This is the basic premises for the proposed research.

Under this investigation, a non-equilibrium plasma at atmospheric pressure is generated to process SO$_2$ and NO$_x$ into products that are easy to remove. The plasma is generated by a dielectric-barrier discharge. Our recent studies have indicated that the efficiency of removal of SO$_x$/NO$_x$ is critically dependent on the uniformity of the dielectric-barrier discharge. A considerable amount of effort has been expended to improve the existing discharge.

EXPERIMENTAL PROCEDURES

The first stage of the research consisted of the design and fabrication of the discharge chamber. The instruments for on-line diagnostics, which consist of emission spectroscopy, residual gas analysis, and SO$_2$ pulsed fluorescence spectroscopy, were put in place. The discharge parameters such as gas flow, gas pressure, gas composition are controlled by a set of mass flow controller and gate valves. This part of the system was tested and was found to perform to satisfaction. The schematic of the experimental setup along with discharge chamber is shown in Fig. 1.
A mass flow controller system was used to mix the gases to form a synthetic flue gas. As opposed to premixed gases, the mass flow controller system has the advantage that the mix can be varied to study the effect of its component on the removal process. The SO$_2$ is detected by a pulsed fluorescent detector capable of detecting SO$_2$ to 1 ppm. A bottle of 500 ppm of NO in nitrogen has been installed in the flow controller system. The NO is detected with a residual gas analyzer on line with the system.

The gas is bubbled through water to add water vapor to the mixture. The premixed gas may be heated up to 300 °C in a coil with a heater. The amount of water vapor present in the gas is measured with a hygrometer which is also capable of measuring the gas temperature.

RESULTS AND DISCUSSIONS

The critical electrical tests on the discharge chamber have been performed. A set of onset voltage versus pressure curves have been obtained for different electrode geometry. The results suggest that for a coaxial geometry a inner electrode with a larger radius needs lower onset voltage. The onset voltage (voltage required for the discharge to be initiated) is shown in Fig. 7 for different values of the inner electrode. Most of our experiments were done with the largest inner electrode possible.

We are able to achieve a stable and uniform discharge by UV irradiation of the dielectric-barrier. The number of microdischarges considerably increases with UV irradiations as shown in Fig. 2. The oscilloscope trace of the voltage and the current of Fig. 2a and 2b correspond to with and without UV irradiation. The intensity of the UV is approximately 10 μW/cm$^2$ in the discharge region, which is a very low value.

The dielectric-barrier discharge is suitable for generating a non-thermal plasma for processing of flue and toxic gases.
The use of very low levels of UV from a mercury lamp changes the discharge characteristics; the discharge is more uniform due the larger number of microdischarges.

We are now able to measure the energy input to the discharge accurately. The Fig. 3 shows the discharge voltage on Y-axis and the charge on X-axis. The area under the closed pattern is the energy input to the discharge per cycle. The product of the energy per cycle and the repetition rate gives the power input to the discharge. The oscilloscope traces were taken under the same conditions in all cases shown except for the presence or absence of UV. From Fig. 3 the energy deposited per cycle is 3 mJ and 2.1 mJ per cycle with and without UV. The discharge was operated at 1 KHz giving a average power of 3 and 2.1 W with and without UV respectively. The energy coupled to the discharge with UV is higher than without UV by approximately 50%. This energy goes into providing excited radicals such as O and OH atoms which are required for removal of SO₂ and NOₓ.

The increase in the energy coupling also increases the light emission from the discharge due to UV irradiation; the atomic oxygen emission line is enhanced. The efficiency of SO₂ removal is strongly dependent on the atomic oxygen production. There is an optimum pressure for a given coaxial geometry at which the emission of the oxygen line is maximum. We have very carefully investigated this dependence and this is shown in Fig. 4. The intensity of the line peaks at a certain pressure which is a function of the gap distance (in this the outer electrode and the dielectric are kept fixed and the inner electrode diameter is varied).

During the last quarter, the experimental investigation of the removal of SO₂ with the improved reactor was started. Shown in Fig. 5 is the fractional conversion of SO₂ as a function of the O₂ concentration. We were able to achieve up to 85% removal in dry air. Due to the drifting of the photomultiplier in the SO₂ meter the percentage removal is off by about 10%. Initial removal is proportional to the O₂ concentration. Further addition of O₂ increases the production of O₃, which is a competing process that uses up atomic oxygen.

The removal process is being studied with water vapor in the air and by varying other parameters. The setup for adding water to the system has been incorporated and a dew point hygrometer (Vaisala) is used to measure the humidity. The stability of the discharge has been studied with the water vapor present and was found to be uniform with UV irradiation for air with H₂O up to 6%. The results of SO₂ and NO removal are too preliminary to be included in this report.

Simulation were carried out to understand the process of NOₓ removal by a dielectric-barrier discharge. The simulation
studies were investigated in order to understand the conditions under which NO removal is possible. Fig. 6 shows the fractional removal of NO as a function of E/N (reduced electric field). Clearly approximately 100 Td will be required to efficiently convert NO to atmospheric nitrogen. The different curves are for different concentration of NO in flue gas, and with higher concentration the field required is higher.

Testing on the improved discharge indicates that it operates at higher E/N's (reduced field). This is useful because the removal of NO requires high electric fields.

The tests include electrical and optical emission spectroscopy for air, pure oxygen, pure nitrogen and, air with CO₂ and SO₂. These tests show that with an attaching gas (O₂, CO₂, and SO₂) the discharge tends to form filamentary microdischarges. However, the use of UV irradiation tends to make the discharge more uniform. The results are encouraging because it shows that under most conditions a uniform atmospheric discharge can be maintained with UV irradiation.

One of the emphasis has been the establishment of a stable discharge which is also optimum in terms of production of oxygen atoms. Shown in Fig. 8 is the relative intensity of two spectral lines as the discharge pressure is varied. This was done for a discharge in O₂ with a frequency of 1 KHz a voltage of 30 kV with UV irradiation and flow rate of 500 SCCM. It is clear that the discharge geometry can be optimized for the production of oxygen atoms at the given operating pressure.

![Graph](image)

Fig. 8. Relative Intensity as a function of pressure for a discharge in O₂ with a frequency of 1 KHz a voltage of 30 kV with UV irradiation and flow rate of 500 SCCM.
The discharge voltage and also the frequency of the pulses play an important role in the species concentration. Shown in Fig. 9 is the relative intensity of two emissions for different applied voltages.

![Graph showing relative intensity as a function of applied voltage](image)

Fig. 9. Relative Intensity as a function of applied voltage for a discharge in O\textsubscript{2} with a frequency of 1 KHz a pressure of 600 Torr with UV irradiation and a flow rate of 500 SCCM.

The dielectric-barrier discharge is suitable for generating a non-thermal plasma for processing of flue and toxic gases. The use of very low levels of UV from a mercury lamp changes the discharge characteristics --- the discharge is more uniform. The light emission from the discharge also changes due to UV irradiation; the atomic oxygen emission line is enhanced. There is an optimum pressure for a given coaxial geometry at which the emission of the oxygen line is maximum. With increase in pulse voltage or frequency of pulsing, the light emission increases. The key to the use of the dielectric-barrier discharge for cleanup is the maintenance of a stable uniform discharge for varied gas composition including trace particle contamination.

The emission spectra of the dielectric-barrier discharge has been studied and the results for oxygen discharge is shown in Fig. 9. The figure shows the spectra with and without UV irradiation. The very large difference in the intensities indicate that there is considerable improvement in the radical production with UV irradiation.

During the last quarter, the experimental investigation of the removal of SO\textsubscript{2} with the improved reactor was started. Initial runs with SO\textsubscript{2} indicates approximately 85% removal of SO\textsubscript{2} at concentration of 5000 ppm in dry air. We are studying
the effect of moisture on the removal of SO$_2$. Several papers in the literature suggest that OH radicals produced by

$$H_2O + e \rightarrow H + OH$$

is very efficient in removing SO$_2$ via

$$SO_2 + 2OH \rightarrow H_2SO_4$$

The removal process will be further studied by varying other discharge parameters.

Testing on the improved discharge indicates that it operates at higher E/N's (reduced field). This is encouraging because the removal of NO will require high electric fields.

We have started a systematic experimental study of the removal of NO. The experiment consist of study of the removal process for parameter variations like gas pressures, gas flow rates, and applied voltage and frequency.

TRACE ELEMENT REMOVAL

It has been proposed that the dielectric-barrier discharge will be very effective in removal of Hg compounds and other trace elements in the flue gas by inducing certain chemical reactions.

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 by the following process;\(^2\)

$$HgS + O_2 \xrightarrow{>700^\circ C} Hg^0 + SO$$

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\[ HgO+C \rightarrow Hg^0 + CO \]

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 through the following mechanism.

\[ O_2 + e \rightarrow O + O + e; Hg + O \rightarrow HgO \]

Also if trace amounts of Cl is present, it may be possible to form Mercury Halides in the discharge which is less hazardous compared to the oxide.

**CONCLUSIONS AND RECOMMENDATIONS**

It is interesting to compare an electrostatic precipitator (ESP) to the electrical scheme proposed here. Typical electrostatic precipitators operate with voltages of 30 to 70 kV, dependent on design factors, and the operating current density is of the order of 50 to 500 nA/cm². The voltage requirements for dielectric-barrier discharge is of the order of 15 - 25 kV ac and currents of the order of 10 µA/cm² of discharge area. The electrical requirements are comparable in both cases. In a EPS system the inlet pressure is of the order of 14.7 psia and the inlet temperature varies between 225 - 900 °F. We are conducting our experiments similar pressures, however to date the experiments were at room temperature and are lower compared to an inlet of an ESP. The published rates for the oxidation reaction suggests that the temperature will not have a drastic effect on the removal process.

In the united states, sulfur trioxide (SO₃) and sulfuric acid are the most successful and widely used conditioning agents for EPS on coal fired utility boilers. The primary mechanism is condensation or absorption on fly ash surfaces. It may also increase the cohesiveness of fly ash. It appears that SO₃ or H₂SO₄ produced by oxidation in the dielectric-barrier

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discharge will be beneficial for ash removal if placed before an ESP.

The key to the use of a dielectric-barrier discharge is the maintenance of a uniform discharge under the adverse condition of a flue gas stream. We are able to achieve this through UV irradiation of the dielectric-barrier discharge.

The results of the study were presented at the EPRI Symposium on Environmental Applications of Advanced Oxidation Technologies. This symposium was jointly sponsored by EPRI and NSF. The main focus of the symposium was on solutions to environmental problems utilizing advanced oxidation technologies. In this symposium several papers were presented on NOx removal using electron beams and nonthermal discharges. The cost effectiveness of using electrical methods was a major topic of discussion, and it was concluded that nonthermal discharges have the potential for application to SOx and NOx removal. Conservative estimates show that for NOx removal, the energy cost would be about 50 ev/molecule.

The PI, at the invitation of Dr. L. Rosocha, visited the Los Alamos National Laboratory and presented a talk on the use of the dielectric-barrier discharge for pollution control. The group at Los Alamos is actively engaged in the use of nonthermal plasmas for removal of VOC. This visit was mutually beneficial as it will result in the exchange of technical information.