

FINAL TECHNICAL REPORT
November 1, 1999, through October 31, 2000

Project Title: **PLASMA-ASSISTED REMOVAL OF SO₂/NO_x/HG FROM
HIGH-SULFUR COAL COMBUSTION GASES**

ICCI Project Number: 99-1/1.2B-2
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ABSTRACT

The objective of the research is to develop a novel process to replace reagents with plasma in a wet scrubber for SO₂/NO/Hg removal. A multi-stage reactor has been fabricated and the system has been tested. The reactor is modular, and additional stages can be added in parallel to scale to larger gas flow. Results have been obtained on power consumption as a function of number of stages. The power consumption increases almost linearly with the number of stages. The SO₂ removal scales linearly with the reactor length, applied voltage to the reactor and the power frequency. The removal also increases with increasing water flow through the reactor.

A slipstream has been designed from the scale-up parameters. The slipstream specifications are for a 10-15 cfm flue gas from a stoker unit at the Southern Illinois University Physical Plant.

The results of the tests on the multistage wet-plasma reactor are very promising. This is the first report of data from a wet plasma scrubber. The removal efficiency is far better compared to the dry plasma techniques being investigated throughout the world.

EXECUTIVE SUMMARY

The objective of the research is to develop a novel process to replace reagents with plasma in a wet scrubber for SO₂/NO/Hg removal. The plasma-based reactor has been developed and fabricated. It consists of four modular reactors in parallel. Additional stages can be easily added to handle increased gas flow without additional pressure drop. We have designed and tested plasma reactors that can flow a maximum of 2 cfm. For efficient plasma generation, the tube diameter is limited to about 2 cm. This limits the flow through each unit. With 6-8 units in parallel, the flow rates of 10-15 cfm can be achieved for the slipstream tests.

We have found that smaller the bead size, the better the mixing. However with smaller size bead, the downward flow of water is impeded and gas bubbles start to form. We chose to go with higher bead size, as a smooth water flow was necessary for the proper function of the reactor.

We have calculated the pressure drop in our reactor for a flow rate: 5000 sccm = 83.3 scfs = 0.0029 ft³/s. With these Assumptions: gas temperature = 311K, Density of gas = 0.072 lb/ft³, and Viscosity = 1.90 x 10⁻⁵ Pa-s the Re > 2200 indicating that there is a turbulent flow. Therefore we may calculate the pressure drop using the orifice equation:

$$\Delta P = C_1 \rho_g U^2$$

Where: ΔP = pressure drop in H₂O/ft packing, C_1 = constant for a packing. Since we are using the glass spheres 5 mm in diameter, we assume $C_1 = 0.8$, ρ_g = gas density, lb/ft³ and U = superficial gas velocity in ft/s. The superficial velocity will be influenced by the fill factor of the packed beads. For hard spheres, assuming closed hexagonal packing, the filled space is approximately 74%. Therefore the superficial velocity will increase, and for annular region of 0.75 inch OD and 0.25 inch ID, the velocity = 8.5 ft/s.

Therefore for our system,

$$\Delta P = 0.8 \times 0.072 \times (8.5)^2 = 4.2 \text{ in H}_2\text{O/ft packing or (7.5 mm of Hg/ft)}$$

The actual pressure drop will be higher due to under estimation of superficial velocity. Different glass bead sizes were investigated for the packed bed dielectric. The three sizes are 3mm, 4mm, and 5mm. We measured the pressure drop across the reactor for these beads. Due to low values of pressure drop, the experimental measurements were not very accurate. We estimate the pressure drop in the range of 3-5 mm of Hg per 2 cm of the reactor height from the largest to the smallest bead. This was done with a tube of 1.6 cm ID. Typical reactor lengths to be expected are about 10 cm. This would result in a pressure loss of 30-50 mm of Hg.

We have studied the power requirement for different number of stages (up to 4). The power requirement is very much a linear function of the number of reactor. The load is highly capacitive typically with a leading power factor of 0.1. Our results indicate that the kVA (reactive power) can be reduced significantly by introducing an inductor in

parallel with the reactor. The load capacitance can be calculated for coaxial reactor geometry. We estimate for four reactors in parallel the capacitance is approximately 1 nF. For an operating frequency of 5 kHz, the required inductance is about 1 Henry.

The removal of SO₂ scales very well with voltage and length of the reactor. Clearly the reactor design lends itself to scaling to handle large flow rates and large SO₂ concentrations. Our current power source is not capable of going up any further to determine the saturation limits.

Removal studies were done for no water flow and with different water flows through the reactor. Data from the CRC physical and chemical handbook shows the solubility of SO₂ in cold water (0 °C) as 22.8 g/cc and in hot water (90°C) as 0.58 g/cc. In room temperature water we see a reduction of SO₂ from 3500 ppm to 2330 ppm with water alone (without plasma). For 240 ml/minute of water flow through the reactor, this amounts to 5.5 mg of SO₂/minute. The concentration of SO₂ in water is 2.3 mg/100 cc of water. Therefore the nearly 30% reduction in SO₂ concentration with water alone is well within the solubility range of SO₂. With the plasma turned on, the removal efficiency falls from 84% to 40% when water flow is stopped. Clearly, the process under investigation with water flow in the plasma is superior to the dry systems being currently investigated by other investigators.

Preliminary results show that there is slight reduction in the removal of SO₂ with a combined flow of 600 ppm NO. This result is to be expected because NO and SO₂ compete for the same radicals (OH) for removal.

Shown below is the design specification for the slipstream:

1. Slipstream flow rate of 10-15 cfm of flue gas at 300-400⁰F.
2. Number of modular reactor required for the above flow rate is 4-6.
3. Water flow rate is 200 ml/minute per cfm of flue gas.
4. Power source of 100-300 V at 1.5 kVA.
5. Transformer 100:1 at rated voltage of 30 kV(RMS) and 1.5 kVA.

The SIU physical plant has several facilities for generating steam and power. It uses Illinois coal #6. Its main facility is based on fluidized bed combustion technology. The SO_x/NO_x concentrations from fluidized bed combustor are low and not suitable for our tests. In addition the physical plant has three stoker units, which are used for additional steam generation during peak season. After meeting with the physical plant managers it was decided that using the flue gas out of the stoker units would meet our specification.

The ductwork consists of 1-inch pipes capable of flows of 10-25 scfm. Since the pressure is negative a fan (Cole-Palmer) is used after the plasma reactor to maintain a flow. A gas chromatograph for the SO₂ and NO_x analysis is part of the on-line diagnostics. This instrument is Gow_Mac 550p equipped with TC (thermal conductivity detector) and Porapak Q columns. The gas at the exit of the reactor is sampled with a six-port VALCO sampling valve.

The flue gas from the boiler (steam capacity of 80 lb/hour at 300°C) goes through an economizer and bag-house and from there to the stack. The slipstream is designed to be right after the boiler. The flue gas temperature is in the range of 400-600°F depending on the load. The expected SO₂ concentration is in the range of 1500-2500 ppm. The NO₂ concentration is in the range of 500-800 ppm. In addition the flue gas at this point has particulates.

As a conclusion, the testing of the modular reactors provided data for the scale-up to slipstream tests. The fractional removal of SO₂ scales linearly with the length of the reactor, the voltage and frequency. Increased flow is handled by increasing the number of reactors without additional pressure drop. This is extremely encouraging for scale-up, since we have not reached saturation levels for the removal of SO₂. As a result of this research, we were the first to show that large quantities of SO₂ removal works better with an wet plasma reactor instead of the dry reactors, which are being investigated by other researchers. A complete set of design specifications were obtained for slipstream tests with a flow of 10-15 cfm.

Funding cycle of 2 years would be needed to perform thorough slipstream tests. A 1-year funding is not adequate to perform reliable slipstream test that can be carried one-step further to pilot plant studies.

OBJECTIVES

The objective of the research is to develop a novel process to replace reagents with plasma in a wet scrubber for SO₂/NO/Hg removal. This technology is capable of removing 90-95% SO₂ in concentrations of 3000 ppm and 90-95% NO in concentrations of 600 ppm. The plasma generates OH radicals, that can efficiently remove SO₂/NO without chemical additives and the resultant byproducts are clean mixed acids. The obvious advantages of this method are (1) it reduces water usage and eliminates solid waste, (2) it simultaneously removes SO₂/NO_x/Hg, and (3) the technology can be retrofitted to existing wet scrubbers. The following tasks were completed during the project period.

Task 1: *Fabrication of modular plasma-reactors*

Task 2: *Determination of the process parameters for SO₂ (3000 ppm) removal*

Task 3: *Determination of the optimal parameters for simultaneous SO_x/NO_x/Hg removal.*

Task 4: *Scale-up and retrofit studies.*

INTRODUCTION AND BACKGROUND

Although a utility can purchase allowances, the Open Market Trading Rule is intended to encourage pollution prevention and source reduction. With the reluctance of the utilities to adopt advanced technology, clearly long-term improvements are needed in pulverized coal combustion technology. This technology will help electrical utilities comply with the 1990 Clean Air Act Amendments (CAAA) while continuing to use high-sulfur Illinois coal

Shown in Fig. 1 is the overall picture of a power plant. We envision that the plasma-wet scrubber will follow the electrostatic precipitator (ESP). Thus the fly ash will be removed before the flue gas enters the scrubber and the byproducts will be liquid. This liquid will be mixed acids, which can be recovered and used in fertilizer industry. Since water can be re-circulated, the process will require less water compared to lime/limestone slurry. In addition, since the ESP precedes the scrubber, the cooling due to the scrubber will not affect its performance. However, the scrubber will need a mist eliminator and

clean gas may have to be reheated for proper dispersion.

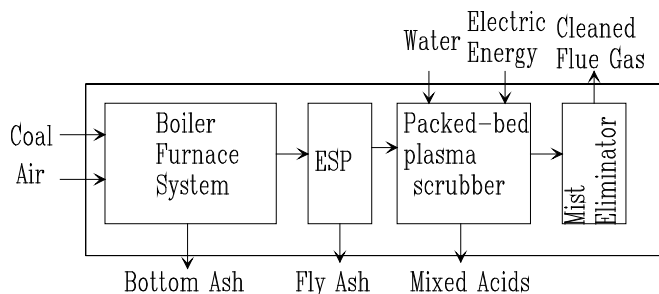
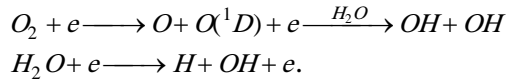


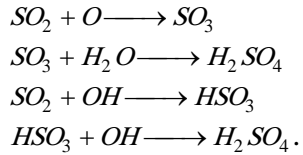
Fig. 1. The packed-bed plasma scrubber with respect to the overall system.

The basic process of removal of SO₂ using a wet plasma scrubber has been demonstrated. The work related to this project is process development. The theoretical basis for the removal of SO₂ is discussed below. In a dielectric-barrier discharge, the dissociation of water and oxygen by electrons produce the hydroxyl radicals and

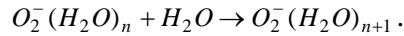
oxygen atoms:



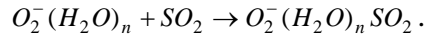
The O and OH radicals react with SO₂ to form H₂SO₄, and the reaction scheme is shown below,



It has been shown that heterogeneous reactions in droplets and clusters are very effective in oxidizing SO₂ and NO to the corresponding acids H₂SO₄ and HNO₃, respectively. The O₂⁻ (the primary negative ion in the discharge) formed in the discharge goes through cluster formation in a step-by-step reaction with water;

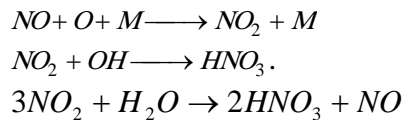


The result of SO₂ penetration in clusters is the formation of a most thermodynamically stable core

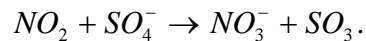


This chain reaction is very effective in oxidizing SO₂. We predict on this basis that in the wet plasma system, the removal of SO₂ and NO will proceed very efficiently.

For the removal of NO, the following reaction scheme is used in the gas phase



In the cluster formation described above, the core ion has a peroxide structure and is a good oxidation agent. The NO₂ oxidation of this ion is as follows,



EXPERIMENTAL PROCEDURES

The schematic of the wet-plasma reactor is shown on Fig. 2. The configuration is a cross flow reactor with the water coming down and the gas moving up. It consists of a glass dielectric (1.6 cm) with the inside filled with glass pellets. The size of the glass pellets

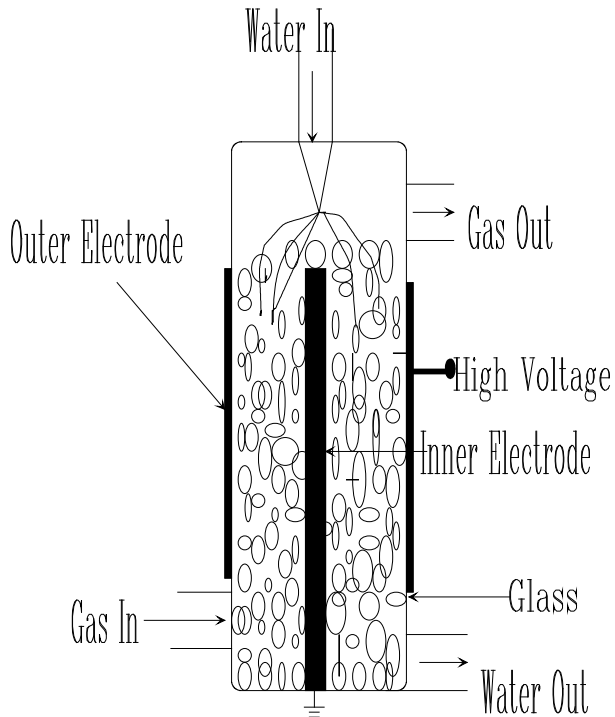


Fig. 2: Schematic of the modular reactor

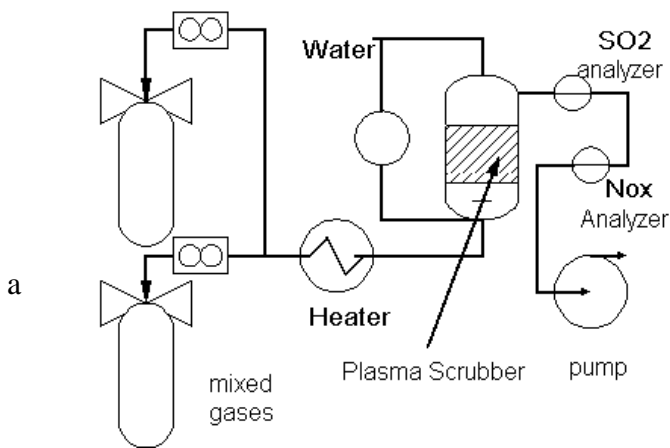


Fig. 3 . Experimental Setup

can be varied (4-5 mm). The inner electrode is a 6mm stainless steel rod and the outer electrode is a conducting film on the outer surface of the dielectric. The water is continuously pumped from a bath to the top of the scrubber forming a closed loop. The plasma is created in the gas, liquid and solid mixture between the beads. This produces a heterogeneous medium and enhances the removal rate considerably.

As shown in Fig. 3, the gas flow, gas composition and the discharge pressure will be controlled by MKS mass flow controller available in the PI's laboratory.

After gas mixing, the gas temperature can be controlled by heater. A simple gas heating system (up to 200 C) is installed immediately following the mass flow controllers. The concentration of the inlet H_2O_g determined by with a dew point hygrometer. The discharge parameters (Table II), and flue

gas parameters (Table III) of interest are shown below.

Table II: Discharge parameter

Parameter	Range
Voltage	20-30 kV
Frequency of the high voltage	50 to 5000 Hz
Gas Pressure	760 to 800 Torr

Table III: Flue Gas Parameter

Parameter	Range
Gas Pressure	760 to 800 Torr
Gas Composition	N ₂ , O ₂ , CO ₂ , H ₂ O, SO ₂ , NO, NO ₂
Gas Temperature	90 to 250 °C
Gas Flow	1000 to 20,000 SCCM

RESULTS AND DISCUSSIONS

Design of wet plasma Scrubber:

The plasma- based reactor has been developed and fabricated. The schematic of multi-stage reactor is shown in Fig.4. In addition, the picture in Figure 5 shows the 4 reactors in parallel operation. It consists of four modular reactors (shown in Fig. 2) in parallel. Additional stages can be easily added to handle increased gas flow without additional pressure drop. We have designed and tested plasma reactors that can flow a maximum of 2 cfm. For efficient plasma generation, the tube diameter is limited to about 2 cm. This limits the flow through each unit. With 6-8 units in parallel, the flow rates of 10-15 cfm can be achieved.

The smaller the bead size, the better the mixing. However with smaller size bead, the downward flow of water is impeded and gas bubbles start to form. We chose to go with higher bead size, as a smooth water flow was necessary for the proper function of the reactor.

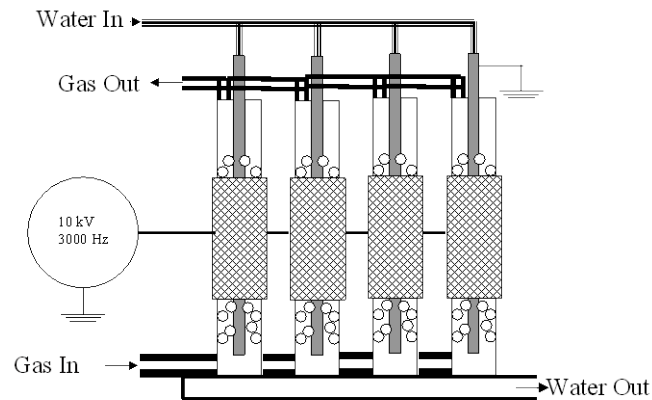


Figure 4: Schematic of the plasma-based reactor. Four identical stages are shown. In this modular design additional stages can be easily added to increase the gas flow.

Pressure Drop in the packed dielectric reactors:

We have calculated the pressure drop in our reactor for a flow rate: 5000 sccm = 83.3 sccm = 0.0029 ft³/s. With these Assumptions: gas temperature = 311K, Density of gas = 0.072 lb/ft³, and Viscosity = 1.90 x 10⁻⁵ Pa-s the Re > 2200 indicating that there is a turbulent flow. Therefore we may calculate the pressure drop using the orifice equation:

$$\Delta P = C_1 \rho_g U^2$$

Where: ΔP = pressure drop in H₂O/ft packing, C_1 = constant for a packing. Since we are



Figure 5: The picture of the plasma reactor. Shown are four identical stages in parallel.

using the glass spheres 5 mm in diameter, we assume $C_1 = 0.8$, ρ_g = gas density, lb/ft³ and U = superficial gas velocity in ft/s. The superficial velocity will be influenced by the fill factor of the packed beads. For hard spheres, assuming closed hexagonal packing, the filled space is approximately 74%. Therefore the superficial velocity will increase, and for annular region of 0.75 inch OD and 0.25 inch ID, the velocity = 8.5 ft/s.

Therefore for our system,

$$\Delta P = 0.8 \times 0.072 \times (8.5)^2 = 4.2 \text{ in H}_2\text{O/ft packing or (7.5 mm of Hg/ft)}$$

The actual pressure drop will be higher due to under estimation of superficial velocity. Different glass bead sizes were investigated for the packed bed dielectric. The three sizes are 3mm, 4mm, and 5mm. We measured the pressure drop across the reactor for these beads. Due to low values of pressure drop, the experimental measurements were not very accurate. We estimate the pressure drop in the range of 3-5 mm of Hg per 2 cm of the reactor height from the largest to the smallest bead. This was done with a tube of 1.6 cm ID. Typical reactor lengths to be expected are about 10 cm. This would result in a pressure loss of 30-50 mm of Hg.

Scaling Studies:

Shown in Fig. 6. is the power requirement for different number of stages (up to 4). The power requirement is very much a linear function of the number of reactor. The load is highly capacitive typically with a power factor of 0.1. Our results indicate that the kVA (reactive power) can be reduced significantly by introducing an inductor in parallel with the reactor. The load capacitance can be calculated for coaxial reactor geometry. We estimate for four reactors in parallel the capacitance is approximately 1 nF. For an operating frequency of 5 kHz, the required inductance is about 1 Henry.

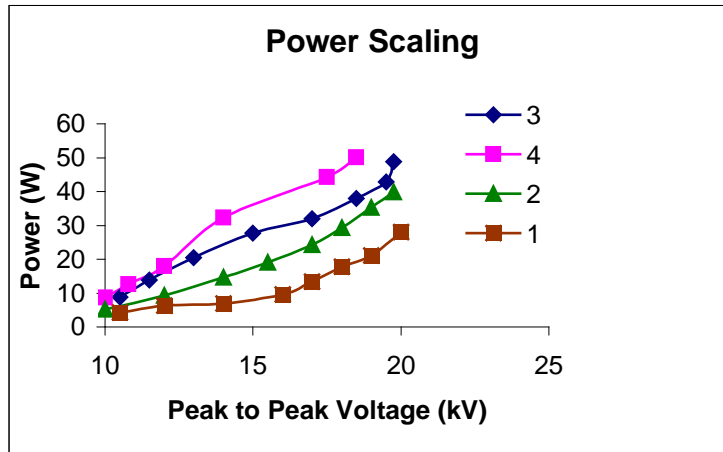


Figure 6: Power required for plasma generation as a function of the number of reactors. This was done at a power frequency of 3kHz.

Figure 7 shows the removal of SO₂ with the wet plasma reactor. The removal scales very well with voltage and length of the reactor. Clearly the reactor design lends itself to

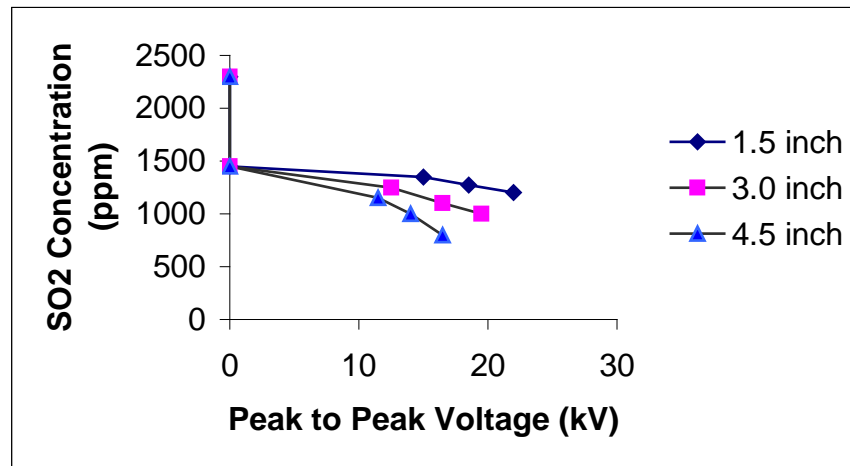


Fig. 7: Removal of SO₂ as a function of applied voltage. The applied frequency=3kHz, and the total gas flow was 15,000 SSCM.

scaling to handle large flow rates and large SO₂ concentrations. Our current power source is not capable of going up any further to determine the saturation limits.

The removal efficiency on water flow was studied extensively and the results are shown in Fig. 8. Removal studies were done for no water flow and with different water flows through the reactor. Data from the CRC physical and chemical handbook shows the solubility of SO₂ in cold water (0 °C) as 22.8 g/cc and in hot water (90°C) as 0.58 g/cc. In room temperature water we see a reduction of SO₂ from 3500 ppm to 2330 ppm with water alone (without plasma). For 240 ml/minute of water flow through the reactor, this amounts to 5.5 mg of SO₂/minute. The concentration of SO₂ in water is 2.3 mg/100 cc of water. Therefore the nearly 30% reduction in SO₂ concentration with water alone is well within the solubility range of SO₂. With the plasma turned on, the removal efficiency falls from 84% to 40% when water flow is stopped. Clearly, the process under investigation with water flow in the plasma is superior to the dry systems being currently investigated by other investigators.

Preliminary results show that there is slight reduction in the removal of SO₂ with a combined flow of 600 ppm NO. This result is to be expected because NO and SO₂ compete for the same radicals (OH) for removal.

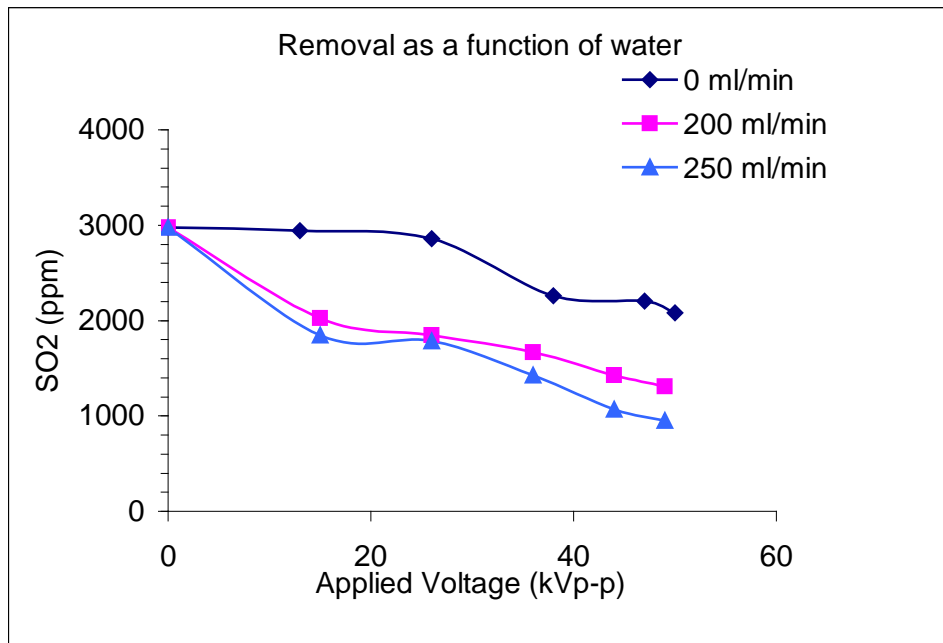


Figure 8: The removal of SO₂ as function of applied voltage for different water flow. The gas flow was at 10,000 SCCM and the source frequency was 1 kHz.

Measurement and Calculation of Acidity

The pH of the water at exit of the plasma reactor was measured with a calibrated pH meter and was found to be 2.2. The corresponding proton concentration is approximately 3.8×10^{-21} /liter of water. The conditions of measurements were,

1. Water flow of 170 cc/min.
2. SO₂ flow of 14.9 SCCM in a total air flow of 5000 SCCM

Assuming that each SO₂ removed produces a H₂SO₄ molecule (2 protons), at 70% removal efficiency the proton concentration is calculated as 3.2×10^{-21} /liter of water. This is in close agreement with measurements.

Slip Stream Design Parameters:

Shown below is the design specification for the slipstream:

1. Slipstream flow rate of 10-15 cfm of flue gas at 300-400⁰F.
2. Number of modular reactors that are required for the above flow rate is 4-6.
3. Water flow rate is 200 ml/minute per cfm of flue gas.
4. Power source of 100-300 V at 1.5 kVA.
5. Transformer 100:1 at rated voltage of 30 kV(RMS) and 1.5 kVA.

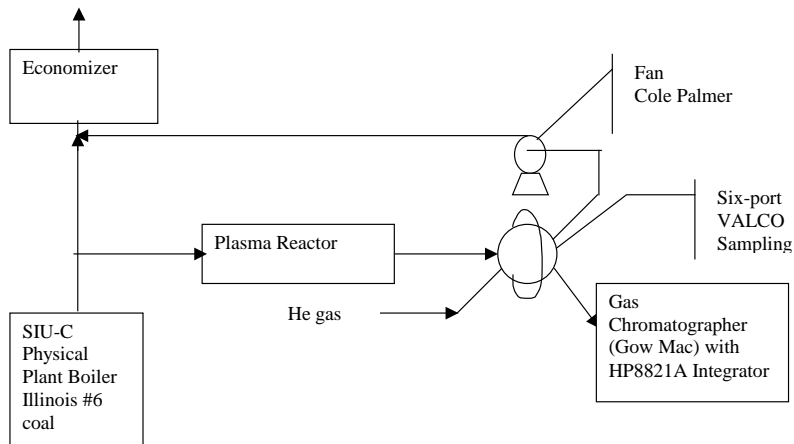


Figure 9: Schematic of the slipstream at the SIUC Power Plant.

The SIU physical plant has several facilities for generating steam and power. It uses Illinois coal #6. Its main facility is based on fluidized bed combustion technology. The SO_x/NO_x concentrations from fluidized bed combustor are low and not suitable for our tests. In addition the physical plant has three stoker units, which are used for additional steam generation during peak season. After meeting with the physical plant managers it was decided that using the flue gas out of the stoker units would meet our specification.

A detailed design of the slipstream is shown in Figure 9. The ductwork consists of 1-inch



Figure 10: The location of the slipstream in the SIUC physical plant

pipes capable of flows of 10-25 scfm. Since the pressure is negative a fan (Cole-Palmer) is used after the plasma reactor to maintain a flow. A gas chromatograph for the SO_2 and NO_x analysis is part of the on-line diagnostics. This instrument is Gow_Mac 550p equipped with TC (thermal conductivity detector) and Porapak Q columns. The gas at the exit of the reactor is sampled with a six-port VALCO sampling valve.

The flue gas from the boiler (steam capacity of 80 lb/hour at 300°C) goes through an economizer and bag-house and from there to the stack. The slipstream is designed to be right after the boiler. Figure 10 shows the actual location of the slipstream. The flue gas temperature is in the range of $400\text{-}600^\circ\text{F}$ depending on the load. The expected SO_2 concentration is in the range of 1500-2500 ppm. The NO_2 concentration is in the range of 500-800 ppm. In addition the flue gas at this point has particulates.

CONCLUSION(S) AND RECOMMENDATION(S)

The testing of the modular reactors provided data for the scale-up to slipstream tests. The fractional removal of SO_2 scales linearly with the length of the reactor, the voltage and frequency. Increased flow is handled by increasing the number of reactors without additional pressure drop. This is extremely encouraging for scale-up since we have not reached saturation levels for the removal of SO_2 . As a result of this research, we were the first to show that large quantities of SO_2 removal works better with a wet plasma reactor instead of the dry reactors, which are being investigated by other researchers. A complete set of design specifications were obtained for slipstream tests with a flow of 10-15 cfm.

The acid concentration was measured and calculated to be around a pH of 2.2. This is a fairly high acid concentration, which can be used for production of fertilizers.

Figure 11 shows a possible configuration of the reactors placed close together in a stack for pilot plant studies. The modularity of the reactors lends itself to easy removal and replacement.

Funding cycle of 2 years would be needed to perform thorough slipstream tests. A 1-year funding is not adequate to perform reliable slipstream test that can be carried one-step further to pilot plant studies.

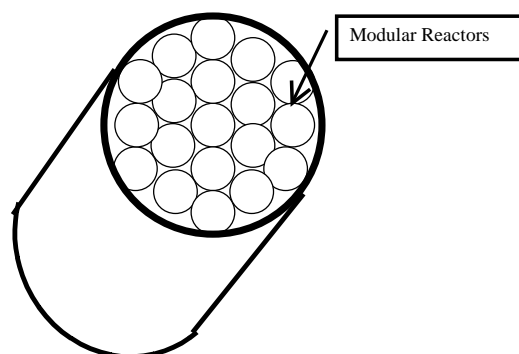


Figure 11: A possible configuration of the reactors for pilot plant studies.

DISCLAIMER STATEMENT

“This report was prepared by Shirshak Dhali, Southern Illinois University, with support, in part by grants made possible by the Illinois Department of Commerce and Community Affairs through the Office of Coal Development and Marketing and the Illinois Clean Coal Institute. Neither Shirshak Dhali, Southern Illinois University nor any of its subcontractors nor the Illinois Department of Commerce and Community Affairs, Office of Coal Development and Marketing, Illinois Clean Coal Institute, nor any person acting on behalf of either:

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