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A NOVEL CARBON-BASED PROCESS FOR FLUE GAS CLEANUP

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ABSTRACT

The objective of this project is to demonstrate the preliminary technical and economic feasibility of a novel carbon-based process for removal of at least 95% SO_2 and at least 75% NO_x from coal combustion flue gas. In the process, flue gas leaving the electrostatic precipitator (ESP) is passed through a trickle bed of activated carbon catalyst employing a periodic flush of low strength sulfuric acid. The SO_2 is oxidized to SO_3 and removed as medium strength sulfuric acid. The SO_2 -free flue gas is then mixed with NH_3 , and the NO_x in the gas is subjected to selective catalytic reduction (SCR) to N_2 over a fixed-bed of activated carbon catalyst.

The project is being carried out over 14 months (June 4, 1991 to July 31, 1992). The experimental work is divided between Research Triangle Institute (RTI) and the University of Waterloo (Waterloo). RTI will conduct the NO_x removal studies, whereas Waterloo will conduct the SO_2 removal studies. The ultimate goal of the project is to demonstrate that the process can reduce the cost of electricity by 20% over conventional SCR/flue gas desulfurization (FGD) processes.

In the present quarter, a detailed project management plan was prepared describing the experimental set-up, work plan and test plan. The experimental equipment is being constructed and is nearly complete with shakedown experiments scheduled to begin on or about November 1, 1991. Also, a paper was prepared and presented for the Seventh Annual Contractor's Conference. The first set of experiments will be completed in the next quarter.

1.0 INTRODUCTION

1.1 OBJECTIVE

The objective of this project is to demonstrate the preliminary technical and economic feasibility of a novel carbon-based process for removal of at least 95% SO₂ and at least 75% NO_x from coal combustion flue gas. The process is based on the demonstrated ability of activated carbons to catalyze SO₂ oxidation and NO_x reduction below 150°C.

1.2 PROCESS DESCRIPTION

The process concept is shown in Figure 1. The hot flue gas leaves the ESP at ~ 150°C and enters a recuperative gas-gas heat exchanger, employing a bed of ceramic balls, to cool the flue gas for SO₂ removal and simultaneously heat the cold flue gas for NO_x removal. The gas leaving the exchanger enters a series of two to three activated carbon trickle-bed catalytic reactors at approximately 100°C to remove the SO₂ and convert it to medium strength sulfuric acid. The essentially SO₂-free gas from the last trickle bed goes through the exchanger to the NO_x converter. The required amount of NH₃ (typically in a NO_x/NH₃ mole ratio of 1) is mixed with the flue gas prior to the activated carbon catalyst bed. The advantages of the proposed process concept compared to currently available SO₂/NO_x processes are summarized in Table 1.

1.3 BACKGROUND

The SO₂ removal process proposed herein is based on the well-known low-temperature catalytic properties of activated carbon, but uses a novel periodically flushed trickle bed to produce a strong acid and a low level of SO₂ in the gas discharge. Hartman et al. (1971) and Hartman and Coughlin (1973) provide a detailed description of the mechanism of SO₂ oxidation [$\text{SO}_2 + (1/2)\text{O}_2 \rightarrow \text{SO}_3$ or $\text{SO}_2 + (1/2)\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$] over activated carbon. The SO₃ formed does not desorb spontaneously at low temperature. It is desorbed with water as sulfuric acid. Sulfuric acid, however, suppresses the ionization of dissolved sulfur dioxide and solubility of oxygen so that countercurrent contacting must be used to continue the reaction at an appreciable rate. Acid formation is accomplished in our process by periodic flushing, which results in a lower pressure drop and more concentrated sulfuric acid than achievable by continuous flushing.

Work in the co-principal investigator's laboratory at the University of Waterloo (Haure et al. 1989) has shown the feasibility of the process. With a single bed and periodic water flushing (0.9 minute water flow in every 90 minute cycle), a time averaged acid concentration of nearly 0.2 molar was achieved. Based on this result, a conceptual process employing acid recycle to produce medium strength sulfuric acid is shown in Figure 2. SO₂ is absorbed from the gas phase and converted into sulfuric acid by two to three in-line periodically liquid-pulsed beds of carbon. Typically water, dilute strength acid or medium

Figure 1. Flue gas cleanup process concept.

TABLE 1. ADVANTAGES OF PROCESS

SO₂ Removal

• Easier retrofit	- Downstream of ESP where space is more readily available
• No waste product	- Sulfuric acid is potentially marketable
• Low temperature	- Reduced equipment stress, non energy intensive, no hazards including carbon combustion
• Simple regeneration	- No carbon loss
• Periodic Operation	- Low pressure drop, concentrated sulfuric acid

NO_x Removal

• High Catalyst Life	- Low temperature operation in the absence of SO ₂ and particles significantly increases catalyst life.
• Low Salt/SO ₃ formation	- Due to complete SO _x removal upstream, the acid dew point of the gas is very low and salt formation is avoided.

**Figure 2. Multi-Bed Periodic-Flushing
Sulfuric Acid Production from Flue Gas**

strength acid flows through them for 2 to 4 minutes in every 30 to 40 minute cycle. The gas phase flows through the beds continuously. Co-current flow is employed so that high superficial velocities can be used without flooding. Two to three in-line, co-current trickle beds of sufficient depth should provide complete removal of SO_2 . The recycling arrangement passes the strongest acid through the bed, treating the richest gas, and thereby produces medium strength acid as a product. The gas-gas heat exchanger brings the flue gas leaving the third bed to the desired temperature for catalytic NO_x removal, which is the second part of our process, as shown previously in Figure 1.

NO_x is reduced in a separate reactor at 120°C using NH_3 after the SO_2 has been removed, and the N_2 and H_2O are vented to the stack. One possible reaction is $4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$, although many others are possible. Many catalysts for the NH_3 - NO reaction are reported in the literature (commercially practiced in SCR technology using vanadium based catalysts). However, many of these catalysts are inactive at 120°C . A comprehensive unpublished review of the literature by the principal investigators indicated that activated carbon or "coke" catalysts are the only catalysts with a potential to carry out the reaction at 120°C . Such catalysts are commercially used in the Mitsui process, which claims some 85% NO_x removal at 130°C . A number of studies (Kusakabe et al. 1988, Kuehl et al. 1986, Seki et al. 1975, U.S. Patent 4,194,373, Kareko et al. 1988) corroborate that activated carbons are active low temperature catalysts for the NO - NH_3 - O_2 and NO - NH_3 reactions. These studies further suggest that activated carbons promoted with very small quantities of group VIII transition metals (particularly platinum) should be considered.

1.4 PROJECT SCOPE/SCHEDULE

The novel carbon-based process to be studied has the potential to provide a technically sound and economically attractive solution to flue gas cleanup. The SO_2 removal experiments will be carried out in the apparatus of Haure et al. (1989) at Waterloo, modified to handle dilute to medium strength sulfuric acid and temperatures up to 100°C . The questions to be addressed in the research include:

- What acid concentrations are attainable by periodic pulsing and acid recycle?
- What is the pressure drop as a function of time during a cycle of no liquid flow to liquid flow?
- What is the optimum size of the granular activated carbon?
- What is the optimum pulse length to prevent poisoning (as occurring in steady state operation) of the activated carbon?
- What is the optimal temperature of operation?
- What will be the effect and fate of NO_x ?

The experimental parameters investigated will include carbon type, size, bed depth, gas composition, liquid composition, gas velocity, liquid velocity, cycle time, flush time and gas temperature. To reduce the number of variables, the carbon used will be the BPL carbon (Calgon Corporation) which was found to be the most active in the previous study. Since the experiments are expected to be short, a large number of parametric experiments will be carried out to prove feasibility and obtain data to permit a process evaluation.

The NO_x removal experiments will be carried out at Research Triangle Institute (RTI). The experiments will be geared toward demonstrating > 75% NO_x removal from off-gases expected from the activated carbon SO₂ conversion process. The principle variables considered will include carbon type (BPL carbon, 0.1 to 1% Pt on carbon, and three others), temperature (100 to 150°C), and space velocity [5000 to 20,000 scf/(cf·h)]. A proper N₂ balance will be carried out in each experiment and slip of NH₃ and NO/NO_x in the reaction products will be measured. Effect of traces of SO₂ up to 250 ppmv on NO_x conversion will be examined.

Based on the experimental data, technical and economic evaluation of the process for 1 MW and 100 MW plants will be carried out. The technical evaluation shall determine the degree of SO₂ and NO_x removal that may be achieved in full-scale plants using the data collected in the controlled laboratory experiments. Economic evaluation will determine the cost of our process on unit power generation basis. The predicted cost will be compared with the cost of the conventional limestone FGD/SCR system. If cost is at least 20% less for our process, our process will be considered for scale-up in future investigations.

The work to be carried out is divided into the following tasks:

	<u>Task</u>	<u>Schedule</u>
Task 1:	Program Definition (RTI and Waterloo)	June 4, 1991 to July 31, 1991
Task 2:	Experimental	August 1, 1991 to May 30, 1992
2.1:	SO ₂ Removal (Waterloo)	
2.2:	NO _x Removal (RTI)	
Task 3:	Process Evaluation (RTI)	May 1, 1992 to July 31, 1992

Task 1 (Program Definition) entails preparation of a detailed Project Management Plan describing a detailed work plan for the entire project and detailed test plans describing the experimental work. In Task 2 (Experimental), facilities will be constructed and experiments will be carried out per the approved Project Management Plan. SO₂ removal experiments will be carried out at Waterloo under the supervision of Dr. P.L. Silveston. NO_x removal experiments will be carried out at the Research Triangle Institute (RTI) under the supervision of Dr. S.K. Gangwal. In Task 3 (Process Evaluation), technical and economic evaluation of

the process for 1 MW and 100 MW plants will be carried out by RTI.

It will be important to maintain a high degree of communication between Waterloo and RTI to assure success of the project. The communication will be maintained by weekly conference calls. Also, an RTI investigator will travel to Waterloo at least twice during the project to review their experimental progress. Similarly, a Waterloo investigator will travel to RTI at least twice during the project.

1.5 MEASURES OF SUCCESS

The targets that we hope to achieve during the course of our experiments are:

- 1) 95% or greater removal of SO_2 ,
- 2) Production of at least 2 molar sulfuric acid,
- 3) Pressure drop of at most 30 inches in the SO_2 removal process,
- 4) 75% or greater removal of NO_x , and
- 5) 25 ppmv or less NH_3 slip.

The experimental data would also indicate how to achieve further improvements in the above targets. The project is designed to prove the technical and economic feasibility of the process and provide sufficient data to permit a preliminary process evaluation. The ultimate test of the success of the project will be whether the process can reduce the cost of electricity over conventional FGD/SCR processes by 20%.

2.0 WORK COMPLETED IN PREVIOUS QUARTERS

This is the first quarterly report for this project, thus no work has been carried out in previous quarters.

3.0 WORK COMPLETED IN PRESENT QUARTER

3.1 ACCOMPLISHMENTS

The accomplishments in the present quarter are as follows:

- A paper was published and presented at the Seventh Annual Coal Preparation, Utilization, and Environmental Control Contractor's Conference sponsored by DOE/PETC;
- Task 1 was completed. A detailed Project Management Plan was prepared describing the work plan, experimental apparatus, experimental test plan/sequence, milestone schedule, cost plan, key personnel plan, project management structure, and measures of success;
- Task 2 was begun. The assembly of experimental apparatus at Waterloo and RTI was nearly completed with shakedown tests scheduled to begin on or about November 1, 1991. Calibration of all analytical instrumentation was nearly completed;
- Sufficient catalyst was procured for the SO₂ removal experiments at Waterloo. For the NO_x removal experiments at RTI, two catalysts have been selected and procured for the initial tests.

3.2 SO₂ REMOVAL

3.2.1 Planned Experimental Facility

Arrangements have been made to construct the experimental equipment in room 2533 Waterloo, Building E1. This is part of a three level research facility equipped with water, air, gas and power. This room is convenient to the chemical engineering workshops, central supply and a computing facility.

The equipment will be constructed on a bench and the vessels will be mounted on a vertical plywood support. All safety and health regulations have been taken into account. Off-gasses will be vented into a fume hood located just several feet from the apparatus. Waste acid will be collected and disposed through the university waste disposal system. The fume hood will be tested by the university safety group to make sure that the draft is adequate.

An Intel 386 PC microcomputer is also located in this lab which will be shared with another project and used for data logging and some control purposes.

A schematic for the proposed apparatus is shown in Figure 3. The apparatus consists of two parts: 1) reactor and 2) feed preparation. Each will be described separately below.

Figure 3. Proposed apparatus for SO₂ removal

3.2.1.1 Reactor

The main part of the proposed apparatus is the 2 inch ID, thick walled glass reactor. The liquid phase (sulphuric acid) and the gas phase (simulated flue gas with 0.25 vol % SO₂) enter the top of the reactor flowing co-currently downward through the reactor. The phases are separated at the bottom and removed separately. The dry simulated flue gas will be 5% O₂ and 15 CO₂ in N₂.

A detailed drawing of the reactor is given in Figure 4. The reactor is made up of a 17 inch long glass cylinder with two glass caps. The top cap adds an additional 2 inches and the bottom adds six inches to the overall height. The caps are flanged and contain o-ring seals. They will be joined to the cylinder with conventional glass clamps. The upper cap contains a quarter inch glass tube at the top for the introduction of the liquid feed. The main glass cylinder contains three - on quarter inch connections, the uppermost for the introduction of the gas feed and two others for manometer connections. The lower glass cap contains a quarter inch gas outlet connection on one side, and a quarter inch connection for the liquid outlet on the very bottom.

As shown in the figure, the upper part of the reactor will be filled with 1/16th inch glass bead as a pre-packing. The purpose of the pre-packing is to distribute the liquid flow. It will also provide mixing of the liquid and gas phases so that they enter the bed at or near equilibrium.

The activated carbon bed rests on a Teflon support screen. Pressure drop will be measured using manometer ports located above and below the bed. Separate measurements using glass beads only will allow for correction so pressure drop across the activated carbon alone can be calculated.

A thorough understanding of the performance requires temperature profile measurements. For this purpose, 1/32nd inch Type K thermocouples covered by 1/16th inch teflon tubing will be used and inserted into the reactor as shown in Figure 4. At each of the three levels, three thermocouples are used in a skewed arrangement so that the axial profiles can be measured at different radial angular positions in the bed. The thermocouple depth is also variable so we will be able to determine the radial temperature profile at three levels.

3.2.1.2 Feed Preparation

The liquid phase will be prepared by diluting laboratory grade 2N sulfuric acid. A large batch of diluted acid will be made and stored so that we can make several runs with the same acid. In order to primarily study the rate and mass transfer of SO₂ in the trickle bed, the gas and liquid phases will be saturated prior to entering the bed.

The liquid phase will pass through a glass gas-liquid contactor that is made of 2 inch ID glass and is four feet in length. As with the reactor, the saturator will be built from three

NOTES

- 1) THE REACTOR IS CONSTRUCTED FROM 2" DIAMETER THICK WALLED GLASS
- 2) ALL CONNECTIONS ARE 1/4"

N.T.S.

Figure 4. SO₂ removal reactor

sections: the two glass caps and a glass cylinder. The top cap will contain a 1/4 inch connection for the liquid feed. Near the top of the main cylinder, a 1/4 inch connection for the air inlet will be added. The air flow will be measured and controlled using a glass rotameter set at a superficial velocity of 1 inch per second. The bottom cap will contain two 1/4 inch connections: the side connection for the air outlet and the bottom connections for the liquid outlet. The main section of the saturator will be filled with 2 feet 6 inches of 1/4 inch glass ballatini supported on a teflon support screen. This is similar to the equipment used by Dr. Haure (1987) which was found to be adequate for phase saturation. This saturator will reduce the interference of mass transfer between the gas and the liquid in the reactor. A two foot 2 inch ID glass separation chamber located after the saturator will ensure that the liquid leaving the saturator will be gas free.

From the separation chamber, the liquid phase will be fed to the overhead gravity feed tank or will be pumped directly into the reactor via a Masterflex pump. The overhead feed tank is a Nalgene 10 litre polypropylene jug that will be supported six feet above the reactor. The feed tank will be open to the atmosphere to ensure that we do not operate much above one atmosphere in the reactor. The feed tank will also contain an overflow line near the top of the tank to ensure that we maintain a constant liquid head. The liquid phase passes from the bottom of the feed tank through a Teflon rotameter to control the liquid flow rate, and then into the top of the reactor. The Masterflex pump will only be used to pump the liquid feed into the reactor if the overhead feed tank does not provide enough flow to the reactor (this could occur for high gas flow rates with small diameter catalyst particles). The liquid flow rate to the reactor will be shut on and off by a solenoid valve working on a timer.

The overflow from the feed tank flows into the top of a Nalgene 50 litre polypropylene holding tank. This tank is filled with the liquid phase to be used during an experimental run. The liquid phase leaves the bottom of the holding tank and is pumped through a Masterflex liquid phase recirculation pump to the gas liquid phase saturator.

The gas phase will consist of a mixture of simulated flue gas and 0.25 vol % SO_2 and 0.05 vol % NO_x for some runs. Simulated flue gas (5% O_2 and 15% CO_2 in N_2) will be obtained by mixing O_2 , CO_2 and N_2 from compressed cylinders using Unit UFC-1100 mass flow controllers. Anhydrous grade SO_2 and NO feed will be provided by a gas cylinder. The flowrates will be measured and controlled with Unit UFC-1100 mass flow controllers.

The experimental apparatus will have the capability to supply either dry gas or water-saturated gas to the reactor. The gas can be saturated with water in a plexiglass column of exactly the same dimensions as the liquid phase saturator and packed with 2 feet 6 inches of 1/4 inch glass ballatini. The gas flow from the saturator then flows to a plexiglass separation chamber of the same dimensions as the glass separation chamber. The gas flow can also bypass the saturator so that dry gas can be used in the experiments to study the effect of mass transfer between the liquid and gas phases in the reactor. Alternatively, the gas can be saturated to minimize any mass transfer occurring between the gas and the water once in the reactor. The gas is then combined with the SO_2 stream and fed to the reactor.

3.2.1.3 Catalyst

The proposed catalyst is activated carbon, type BPL, produced by the Calgon Corporation, Pittsburgh. We propose to use two particle sizes (outlined in the experimental test plan). Data on the catalyst and the bed are presented in Tables 2 and 3, respectively.

The carbon will be boiled in deionized water for about two hours to eliminate fines. The catalyst particles will be deposited sequentially in layers, compacted and vibrated from the outside of the reactor wall to achieve the bed porosity specified by the manufacturer. The bed is supported by a Teflon screen.

TABLE 2. PROPERTIES OF ACTIVATED CARBON CATALYST

Type	:	BPL Calgon Corporation
Raw Material	:	Bituminous Coal
Activation	:	High Temperature Steam
Mesh Size	:	4 x 6 6 x 16
Average Size	:	1/8" 1/16"
Surface Area (BET Method)	:	1050 - 1150 m ² /g
Particle Density (Hg Displacement)	:	0.8 g/cm ³
Real Density (He Displacement)	:	2.1 g/cm ³
Particle Porosity	:	0.6
Bed Porosity	:	.39

TABLE 3. PROPERTIES OF CATALYTIC BED

Cross Sectional Area	:	3.04 in ²
Reactor Inside Diameter	:	2 inches
Height of Bed	:	6 1/2 inches
Volume of Bed	:	19.76 in ³

3.2.2 Work Completed

For the first quarter of our contract, after approval of the work plan, we commenced ordering and constructing the necessary equipment for our experimental apparatus. No experimental work has been done at this time; however, we have started shakedown runs using only water and air in our apparatus.

The construction of the reactor, saturators and separation vessels was done by University of Waterloo technicians. All glassware was built by the resident glass blower. The glassware includes the SO₂ oxidation reactor, a liquid-gas contactor and liquid-gas disengagers. All glassware has been built in pairs to reduce the amount of experimental downtime due to equipment breakage.

A plexiglass saturator was built in the Chemical Engineering machine shop. The reactor, saturator and separation vessels were built according to the specifications given in the proposed workplan.

The equipment has been erected in room 2533, University of Waterloo, building E1. All the piping connections were made by J. Metzinger in a layout congruent with the process flow sheet in the work plan.

A plexiglass shield was constructed around all glass vessels to protect personnel from flying glass in case of glass breakage during experimentation.

Installation of the thermocouples into the glass reactor presented quite a challenge. 1/32nd thermocouples are surrounded by 1/16th O.D. teflon tubing to protect the stainless steel from corrosion. The thermocouples are held in place with special glass and teflon fittings. This arrangement does allow the thermocouples to be moved to different radial depths in the reactor bed.

The computer control system has been purchased and is ready for thermocouple data logging. An aluminum box has been constructed which completely surrounds the computer control system. This was done for safety and security reasons.

The mass flow controllers have been purchased, but we are waiting for delivery. A flow controller has been included for CO₂. The simulated flue gas will therefore be a mixture of 15% CO₂, 5% O₂, 2500ppm SO₂, 500ppm NO for some runs, with the balance being N₂. Once the flow controllers arrive, they will be calibrated and incorporated into the computer control system. The arrival of the flow controllers may be the only major delay to the start of our experiments; however, we expect them to arrive at any day now.

An autotitrator has also been purchased, and we are waiting for delivery. Readings from the autotitrator will be input into the computer system for data logging via an RS232 communication link. The arrival of autotitrator will not cause any delays in the start of experiments since titrations can initially be done manually. Calgon Corporation has supplied us with 5 gallon drums of activated carbon which we will use for our experiments. 2N sulfuric acid which will be diluted for some of our experiments is available in the Chemical Engineering Stores.

At present, we are doing shakedown runs using just air and water. We are doing this to familiarize ourselves with the equipment and to make some initial pressure drop studies of the reactor packed with glass beads (which will be used as the pre-packing) without the catalyst. There have been no problems with the equipment thus far. The tests are being conducted using gas rotometers since the mass flow controllers have not arrived yet. Initial pressure drop results are shown below:

Pressure Drop (mmHg)	Liquid Flowrate (cm/s)	Gas Flowrate (cm/s)
9	1.0	16.35
5	1.0	5.65
1	0.2	5.65
2.5	0.2	16.35

At this time a suitable gas analyzer has not been selected. However, in the interim we will use an FTIR that is available on a temporary basis.

At this time the equipment is running well and we hope to start some preliminary experimental runs with air and SO₂. We have approval to use the equipment from the university safety committee. We will run with only air and SO₂ until the mass flow controllers arrive.

3.3 NO_x REMOVAL

3.3.1 Planned Experimental Facility

The experimental equipment will be housed in Lab 134 of the Research Triangle Institute's Bacon Street High-Bay Laboratory Facilities managed by the Center for Process Research (CPR). This building has 6 high-bay labs, an on-site machine shop and a welding shop. State-of-the-art equipment is available to carry out the proposed experimental work. All health and safety regulations have been taken into account. Off-gases will be vented into a fume hood. Waste condensate will be disposed as aqueous waste through the RTI waste disposal system.

A schematic of the proposed apparatus is shown in Figure 5. The apparatus consists of two parts: 1) reactor and analysis system, and 2) feed preparation.

3.3.1.1 Reactor and Analysis System

The system consists of a single-zone furnace which can house reactors up to 1" diameter. The premixed simulated flue gas enters the bottom of the reactor. The reactor will be made from a 2 cm O.D., 1.76 cm I.D., Pyrex standard wall tubing, 51 cm long. Each end of the tube will be reduced to 1/4" with a tapered connection to allow the use of standard fittings at the ends. The catalyst bed (~10 cm long) will be placed at the middle of the tube, supported on glass wool. The wool will act as flow distributor as well as pre-heater to bring the gases to the required temperature.

A 1/16" thermocouple will be inserted from the top and positioned at the middle of the catalyst bed. The catalyst bed will consist of catalysts ranging in size from 1/16" (0.16 cm) to 3/32" (0.24 cm). A total simulated gas flow of 2 to 8 slpm will be used to provide space velocities ranging from 5000 to 20,000 scc/(cc·h). A thermocouple will also be placed at the gas inlet to the catalyst bed through the wool distributor. The gases leaving the reactor will pass through a condenser pot to knock out the water and an analytical system consisting of a continuous NO_x analyzer, a NH₃ impinger/ion selective electrode, and a GC/TDC. The gases will then be passed through a bubble flow meter for total flow measurement and vented through the fume hood.

3.3.1.2 Feed Preparation

The total gas flows (including vaporized water and NH₃) will range from 2 to 8 slpm. To provide this rather wide flow range, two sets of two flow controllers rated for high flow and low flow will be used. After blending, typically a gas containing 500 ppmv NO, 10% H₂O, 10% CO₂, 500 ppmv NH₃, 5% O₂ and balance will be generated. In some later experiments, SO₂ up to 250 ppmv will be blended in the gas to study catalyst deactivation and/or salt formation with SO₂. Nearly all the SO₂, however, is expected to be removed by our upstream SO₂ removal process. To blend SO₂, the CO₂/O₂ cylinder will be replaced with

Figure 5. RTI NO_x reduction reactor system

a required mixture of SO_2 , CO_2 and O_2 .

The simulated NO-containing off-gas from our SO_2 removal process mixed with the required amount of NH_3 will be generated using two differential flow controllers and a liquid positive displacement syringe pump. Flow controllers will be used to accurately mix the gases. The gas cylinder feeding one of the flow controllers will contain a dry CO_2/O_2 free gas with the required proportion of NO in He, whereas the gas cylinder feeding the other flow controller will contain a dry N_2 -free CO_2/O_2 mixture in the required proportion. There are two important points to note:

- The CO_2 and O_2 are kept in a separate cylinder from the NO cylinder because of the known problem of NO oxidation in a high pressure cylinder.
- NO is contained in He so that during the actual runs, no N_2 is fed to the reactor system. By measuring the N_2 formed from the NO/ NH_3 reaction, a N_2 mass balance will be obtained which will be a backup of the data for NH_3 slip and unconverted NO_x measured independently. This procedure will provide a high degree of data quality assurance/control.

After mixing, the gases will be passed through a pre-heater prior to blending them with the required amount of NH_3 and water vapor. An ammonium hydroxide solution of required NH_3 to water ratio will be pumped using a positive displacement syringe pump at a required flow into the above pre-heater. The pre-heater containing glass beads will be used to properly mix the gases and introduce them into the tubular reactor containing the distributor packing and the required catalyst.

3.3.1.3 Catalyst

The catalyst bed dimensions are shown in Table 4.

TABLE 4. PROPERTIES OF CATALYST BED

Reactor I.D.	:	1.76 cm
Bed Height	:	10 cm
Bed Volume	:	24.33 cm^3
Bed Porosity	:	~ 0.4
Catalyst Size	:	0.16 to 0.24 cm

The bed will be prepared by repetitively adding small quantities of the catalyst and tapping and vibrating the reactor wall. Activated carbon obtained from manufacturers will be the preferred catalyst. However, no fines or powders will be tested. All catalysts tested will be in the 1/16" to 3/32" size range.

3.3.2 Work Completed

Design of the experimental system is complete and construction is nearly complete. A schematic diagram of the test system was shown in Figure 5.

Feed gas concentrations for initial testing consists of 5% oxygen, 10% carbon dioxide, 10% water vapor, 500 ppm nitric oxide, and 500 ppm ammonia in a helium balance. These concentrations are produced by blending individual compressed gases containing $\text{CO}_2 + \text{O}_2$, NO in helium, and pure helium, and then mixing with steam and ammonia generated by vaporizing an ammonia in water solution. The compressed gas flows are controlled by differential flow controllers and monitored by calibrated rotameters. The range of the flow controllers allows testing with 1 SLPM to 20 SLPM total flow. A multi-port valve is used to select either high flow control or low flow control for the helium diluent. An additional selection is provided for a catalyst activation gas which is controlled by a standard rotameter with integral needle valve.

A dual channel syringe pump is used to inject the ammonia in water solution. The solution is injected into a glass pre-heater packed with 3 mm glass beads. After vaporization, the steam and ammonia will be mixed with the other feed gases.

The test reactor consists of a borosilicate glass tube which is 20 mm OD with a 1.2 mm wall thickness. The overall reactor length is 51 cm and has 7.6 cm long stubs on each end, which are tapered to 13 mm OD. The reactor is packed with a selected carbon catalyst supported on a bed of borosilicate glass wool. Thermowells are located at each end of the reactor tube to allow monitoring of the inlet and bed temperatures. The reactor tube is housed in a split tube furnace.

Reactor exit gas passes through a water cooled condenser and trap before exiting the system through a pressure control valve and bubble flow meter.

A three-way valve is located downstream of the reactor to select whether reactor inlet or reactor outlet gas is passed to the analysis manifold.

A Thermo Environmental Instruments chemiluminescent NO_x analyzer has been installed and tested for analysis of nitric oxide. During tests, sample gas is extracted before the condenser at a flow rate of about 1 SLPM. Sample gas passes through a heated sampler in which the pressure (and thus the dew point) is reduced. This allows the measurement of NO without removal of the water vapor.

An Orion ion specific electrode for ammonia has been calibrated with standards prepared from ammonium chloride. To test for ammonia during a run, sample gas is extracted before the condenser at a flow rate of 50 sccm and passed through a midjet impinger containing 25 mL of deionized/distilled water. The ammonia electrode is then used to determine the ammonia concentration in solution, from which the gas phase ammonia concentration is calculated. This method was tested by sampling from a 1050 ppm NH_3 in N_2 standard for 30 minutes at 50 sccm. The concentration based on analysis of the impinger catch with the ammonia electrode was 1112 ppm (+5.9% difference).

A Carle gas chromatograph with a thermal conductivity detector has been calibrated for measuring CO_2 , O_2 , and N_2 from the test system. Two columns have been installed for performing the required separations. The first column is a 9 ft. x 1/8 in. stainless steel tube packed with Hayesep R porous polymer. The second column is a 6 ft. x 1/8 in. stainless steel column packed with 40/60 mesh molecular sieve 5A. A Carle 10-port gas switching valve is used for injection of gas samples and to control the sequence of columns used during the analysis. After injection of a 1 mL sample loop, O_2 and N_2 pass through the Hayesep column and into the molecular sieve. CO_2 is retained in the Hayesep. After one minute, the Carle valve is switched to reverse the column sequence. CO_2 elutes from the Hayesep column first and is detected by the TCD. O_2 and N_2 are separated on the molecular sieve column and then pass through the Hayesep column to the TCD. A Hewlett-Packard 3392A integrator is used for data acquisition and for controlling valve switch timing through an HP-19405A sampler/event control module.

Sample flow through the GC sample loop is provided by adjusting the pressure control valve located just before the bubble flow meter to produce sufficient system pressure (approximately 5 psig).

A number of catalyst suppliers have been contacted to obtain samples that could be used for the $\text{NO} + \text{NH}_3$ reaction. To date, only the following have indicated a willingness to supply samples:

Mitsui Mining/DMT. Bergan-Forschung, which developed the carbon for NO reduction, has been acquired by DMT. They have agreed to supply a sample of their D 52/4 carbon catalyst, but we have not yet received it. Their NO_x -control process uses a carbon that is designed for fluid beds, and Mitsui indicates that it may not be suited for the fixed bed tests we plan to run.

Degussa. Degussa has supplied us with a 1% Pt/carbon catalyst. We have requested, but not yet received, a 1/2% Pt/carbon catalyst.

Calgon. Calgon has sent us two samples of their BPL carbon, which is a standard production item. One of them is a 6 x 16 mesh granulated material. The other is in the form of 1/8" pellets, and is called Xtrusorb 635, Lot A - 08060.

4.0 WORK PLANNED FOR NEXT QUARTER

4.1 SO₂ REMOVAL

Upon arrival of the mass flow controllers, it will take 1 week to incorporate them into the experimental setup. This entire quarter will be used for the first set of 48 experiments. We hope to start experiments by October 21st and be able to run at least one experiment per day. If there are any delays beyond this, we will contact the DOE through RTI immediately. The planned schedule for experiments this quarter is:

October 21 to November 5	First block of 12 experiments
November 5 to 11	Turnaround
November 11 to 26	Second block of experiments
November 26 to December 2	Turnaround
December 2 to 17	Third block of experiments
December 17 to 23	Turnaround
December 23 to January 15	Fourth block of experiments

The turnaround involves the change in catalyst size or sulfuric acid concentration.

4.2 NO_x REMOVAL

The shakedown experiments will begin on November 1, 1991, and we hope to have the system fully operational by December 1, 1991. The planned schedule of experiments this quarter is:

December 1 to December 20	BPL Carbon tested at 3 temperatures and 3 space velocities
December 21 to January 15	Pt-impregnated carbon tested at 3 temperatures and 3 space velocities

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