A NOVEL CARBON-BASED PROCESS FOR FLUE GAS CLEANUP

Third Quarterly Technical Progress Report
January 1 to March 31, 1992

Contract No. DE-AC22-91PC91345
Ms. Diane Revay Madden: DOE COR

Submitted to:

U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940, Pittsburgh, PA 15236

S.K. Gangwal, Project Manager
Research Triangle Institute
Research Triangle Park, NC 27709
(919) 541-8033

P.L. Silveston, Co-Principal Investigator
University of Waterloo
Waterloo, Ontario, Canada N2L3G1
(519) 885-1211, Ext. 2534

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

April 1992

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

Section		Page
	List of Tables and Figures	ii
	Abstract	iii
1.0	INTRODUCTION	1
	1.1 Objective	1
	1.2 Process Description	1
	1.3 Background	1
	1.4 Project Scope/Schedule	4
	1.5 Measures of Success	6
2.0	WORK COMPLETED IN PREVIOUS QUARTERS	7
3.0	WORK COMPLETED IN PRESENT QUARTER	8
	3.1 Accomplishments	8
	3.2 SO ₂ Removal	8
	3.2.1 Equipment Modifications	8
	3.2.2 SO ₂ Removal Experiments at 21 °C	8
	3.2.3 Efforts to Increase Catalyst Activity	11
	3.3 NO _x Removal	14
4.0	WORK PLANNED FOR NEXT QUARTER	19
	4.1 SO ₂ Removal	19
	4.2 NO _x Removal	19
	4.3 Process Evaluation and Publications	19
5.0	REFERENCES	20

LIST OF TABLES

Table 1	Advantages of Process	2
Table 2	Common Experimental Conditions for SO ₂ Removal Tests at 21 °C	10
Table 3	SO ₂ Removal Test Results at 21 °C on BPL Carbon with Inlet Gas Containing 2,500 ppm SO ₂	10
Table 4	Effect of Inlet SO ₂ Concentration on SO ₂ Removal and Conversion at 21 °C on BPL Carbon (Cycle Time = 5 min; Flush Duration = 0.5 min)	11

LIST OF FIGURES

Figure 1	Flue gas cleanup process concept	1
Figure 2	Multistage activated carbon scrubbing process with pulsed liquid flow and cooling of the feed gas and reheating of the off-gas by heat recovery	3
Figure 3	Sampling system for SO ₂ analyzer	9
Figure 4	NO conversion on modified carbon catalyst (space velocity = 1370 scc/(cc•h) [3005 scc/(g•h)]; inlet NO = 530 ppmv)	16
Figure 5	NO conversion on modified carbon catalyst (space velocity = 1370 scc/(cc•h) [3005 scc/(g•h)]; inlet NO = 530 ppmv; NH ₃ /NO = 1.42)	16
Figure 6	NO conversion on modified carbon catalyst (space velocity = 1758 scc/(cc•h) [3948 scc/(g•h)]; inlet NO = 530 ppmv; NH ₃ /NO = 1.25)	18
Figure 7	NO conversion on various carbon-based catalysts (85 cc bed; 1400 scc/(cc•h); 15.7 psia; 5% O ₂ , 10% CO ₂ , 10% H ₂), 75% inert; 530 ppm NO in; NH ₃ /NO = 1.22)	18

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 previous two quarters, a detailed project management plan was prepared describing the experimental setup, work plan, and test plan. A paper was prepared for and presented at the Seventh Annual Contractors' Conference. The experimental system, with the exception of a continuous SO_2 analyzer at Waterloo, was completed for SO_2 conversion at Waterloo and for NO_x conversion at RTI. Shakedown experiments were completed. Scoping studies at Waterloo with the BPL carbon showed that periodic flushing tests could only achieve up to 40% SO_2 removal with one bed. NO_x conversion tests at RTI showed that at about 130 °C, 75% conversion could be achieved at a space velocity of about 700 scc/(cc·h).

In the present quarter, the continuous SO_2 analyzer system at Waterloo was completed. The SO_2 removal factorial experiments were begun at Waterloo with the BPL carbon at 21 °C. Also, SO_2 removal was tested on two catalysts at RTI at 80 °C. NO_x conversion was tested on a variety of catalysts at RTI. It was shown that the BPL carbon could remove over 95% SO_2 at 21 °C but would require several beds at space velocity in each bed of about 1,500 scc/(cc·h) to reduce SO_2 from 2,500 ppm to 100 ppm. A modified carbon catalyst tested at RTI showed 99% SO_2 removal at 80 °C at 1,400 scc/(cc·h). Also, it was possible to produce nearly 9 normal H_2SO_4 by periodic flushing of this catalyst. The modified carbon catalyst also demonstrated removal of more than 80% NO_x at around 140 °C and 1,400 scc/(cc·h). A number of other catalysts were also tested.

Work in the next quarter would include factorial experiments with BPL carbon and the modified carbon catalyst at Waterloo. At RTI, catalyst optimization would continue to reduce the cost of the process. Higher space velocities up to 10,000 scc/(cc·h) will be tested on the optimized catalysts. A preliminary economic evaluation will be conducted and a project review meeting will be held. Also, papers will be prepared for the AIChE meeting in Minneapolis and for the Contractors' Review Meeting.

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% SO_2 and at least 75% NO_x from coal combustion flue gas. The process is based on the demonstrated ability of activated carbons to catalyze SO_2 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 electrostatic precipitator (ESP) at ~150°C and enters a recuperative gas-gas heat exchanger, employing a bed of ceramic balls, to cool the flue gas for SO_2 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 SO_2 and convert it to medium strength sulfuric acid. The essentially SO_2 -free gas from the last trickle bed goes through the exchanger to the NO_x converter. The required amount of NH_3 (typically in an NO_x/NH_3 mol 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 SO_2/NO_x processes are summarized in Table 1.

Figure 1. Flue gas cleanup process concept.

1.3 BACKGROUND

The SO_2 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

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, nonenergy 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
-
-

produce a strong acid and a low level of SO₂ in the gas discharge. Hartman et al. (1971) and Hartman and Coughlin (1972) 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 (Waterloo) (Haure et al., 1989) has shown the feasibility of the process. With a single bed and periodic water flushing (0.9 min water flow in every 90-min 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

Figure 2. Multistage activated carbon scrubbing process with pulsed liquid flow and cooling of the feed gas and reheating of the off-gas by heat recovery.

periodically liquid-pulsed beds of carbon. Typically water, dilute strength acid or medium strength acid flows through them for 2 to 4 min in every 30- to 40-min 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 selective catalytic reduction (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 the 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. Because 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 SO_2 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 [5,000 to 20,000 scf/(cf·h)]. A proper N_2 balance will be carried out in each experiment and slip of NH_3 and NO/NO_x in the reaction products will be measured. The effect of traces of SO_2 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 SO_2 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 fluid gas desulfurization (FGD)/SCR system. If cost is at least 20% less for our process, our process will be considered for scaleup 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. SO_2 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 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 ensure 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:

- 95% or greater removal of SO_2 ,
- Production of at least 2 molar sulfuric acid,
- Pressure drop of at most 30 in. in the SO_2 removal process,
- 75% or greater removal of NO_x , and
- 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

The accomplishments in the previous quarters were as follows:

- A paper was published and presented at the Seventh Annual Coal Preparation, Utilization, and Environmental Control Contractors' Conference sponsored by the U.S. Department of Energy/Pittsburgh Energy Technology Center (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 and shakedown tests at Waterloo and RTI were completed with the exception of the installation of a continuous SO₂ analyzer.
- Sufficient catalysts were procured for the SO₂ removal experiments at Waterloo and for the NO_x removal experiments at RTI.
- A number of catalyst screening tests were completed for SO₂ and NO_x conversion. It was shown that 75% NO_x conversion was possible on selected carbon catalysts.

3.0 WORK COMPLETED IN PRESENT QUARTER

3.1 ACCOMPLISHMENTS

The accomplishments in the present quarter are as follows:

- A continuous SO₂ analyzer system was commissioned at Waterloo and SO₂ removal factorial experiments with BPL carbon at 21 °C began.
- SO₂ removal was also tested at RTI on a modified carbon catalyst and a CarboTech carbon at a higher temperature (80 °C). CarboTech carbon is the same as the material used in the Mitsui-BF process.
- NO_x removal was tested at RTI on a number of carbon-based catalysts.
- It was shown by Waterloo that the BPL carbon could remove 95% SO₂ at 21 °C but would require several beds at a space velocity of 1,500 scc/(cc·h).
- The modified carbon catalyst tested at RTI consistently removed 99% SO₂ over multiple cycles at 80 °C and 1,400 scc/(cc·h). Periodic flushing showed the potential to produce up to a normal sulfuric acid without a concentration step.
- The modified carbon catalyst also demonstrated removal of more than 80% NO_x at about 140 °C and 1,400 scc/(cc·h).
- An abstract was submitted to the Coal Combustion Flue Gas Cleanup Symposium at the Minneapolis AIChE meeting.

3.2 SO₂ REMOVAL

3.2.1 Equipment Modifications

A continuous SO₂ analyzer was installed for Waterloo's SO₂ removal apparatus. A schematic of the sampling system is shown in Figure 3. Also, RTI's NO_x removal reactor system was configured so that it could be used for either SO₂ removal or NO_x removal with only a small downtime prior to changeover. The reason to reconfigure RTI's equipment was so that elevated temperature runs could be made for SO₂ removal. Waterloo's equipment has the capability for periodic liquid flushing with continuous gas flow at all times. RTI's equipment requires physically removing the reactor to flush it with liquid and putting it back on line for the next SO₂ removal cycle.

3.2.2 SO₂ Removal Experiments at 21 °C

These experiments were conducted by Waterloo. The SO₂ analyzer continuously measures removal of SO₂. Experiments done last quarter, without the SO₂ analyzer, utilized

Figure 3. Sampling system for SO₂ analyzer.

wet chemistry methods to indirectly determine SO₂ removal by measuring the acid strength of the liquid flush. The two methods have differed by only 5 to 10%.

Common experimental conditions for the 21 °C experiments at Waterloo are shown in Table 2. All experiments utilized the "as received" BPL carbon from Calgon Corporation. The experiments involved exposure of the carbon bed to an SO₂ containing flue gas saturated with water at 21 °C for a certain time followed by a periodic water flush. The gas flowed through the catalyst continuously, even during the water flush. Cycle time was defined as the time period from the time of the start of a water flush to the start of a subsequent water flush. Liquid flush duration and cycle time were varied to attempt to find optimum points of SO₂ removal and acid strength produced.

The results of SO₂ removal experiments with a 2,500 ppm SO₂ feed are shown in Table 3. SO₂ removal is below 40% at the conditions tested. Furthermore, the carbon appears to lose activity with continued testing. For example, test T4 is a duplicate of T1. Yet, the SO₂ removal is only 25.1% as opposed to 37.4%. SO₂ removal with continuous flushing is not much better—only 40.0%—and a lower acid strength is produced. SO₂

Table 2. Common Experimental Condition for SO₂ Removal Tests at 21 °C

Bed size	177.92 g, 360 cc
Bed diameter	2 in. (5.08 cm)
Bed depth	7 in. (17.78 cm)
Catalyst	4 × 6 Mesh, BPL catalyst
Volumetric dry gas composition	CO ₂ = 15%, O ₂ = 5.0%, N ₂ = balance, NO _x = 0.0
Superficial gas velocity	5.65 cm/s
Superficial liquid velocity	0.2 cm/s
Flushing liquid acidity	0 mol/L (water)
Pressure drop	
without flush	0.53 in. of H ₂ O
with flush	1.07 in. of H ₂ O

Table 3. SO₂ Removal Test Results at 21 °C on BPL Carbon with Inlet Gas Containing 2,500 ppm SO₂

Test no.	T1	T1 duplicate	S1 continuous	T2	T3	T4	T5	T6	T6 duplicate
Cycle time (min)	30	30	continuous	15	5	30	60	5	5
Flush duration (min)	3	3	--	3	0.5	3	0.6	0.5	0.5
Average SO ₂ removal (%)	37.4	39.0	40.0	40.1	34.5	25.1	15.0	26.8	28.6
% SO ₂ removal converted to H ₂ SO ₄	--	--	--	--	--	49.4	--	23.7	26.7
Average acidity (mol/L)	0.0094	0.0098	0.0046	--	0.009	0.007	0.043	0.008	0.008

removal increases slightly by reducing the cycle time and flush time (for example, compare T6 results with those of T5 and T4). Measurement of SO₃ in the liquid indicates that only a fraction of SO₂ that is removed is converted to SO₃ and subsequently to H₂SO₄. This result suggests that the SO₂ is adsorbed on the carbon surface at the low operating temperature and is partly flushed out by the water as H₂SO₃. Some of the adsorbed SO₂ is oxidized to SO₃ and is flushed out as H₂SO₄.

The above results showed insufficient catalyst activity to enable 95% SO₂ removal using a single bed. To demonstrate, however, that 95% removal can be achieved with a

deeper bed or multiple beds, a series of experiments were conducted in which the inlet SO_2 concentration was reduced to a level where 95% removal could be achieved with the existing BPL carbon bed. These results are shown in Table 4 and show that more than 95% removal is possible with a 600 ppmv inlet SO_2 under the same conditions. Also, nearly all of the SO_2 removed is converted to H_2SO_4 for the 600 ppmv SO_2 run. This result demonstrates that the required removal can be achieved with multiple beds of BPL carbon.

3.2.3 Efforts to Increase Catalyst Activity

The above results suggested that 95% SO_2 removal could be achieved with the BPL carbon. However, several beds would be required. This may not be economical and thus efforts were made to increase the catalyst activity.

Catalyst activity could be increased by (1) activating the BPL catalyst, (2) using a more active catalyst, or (3) using a higher reaction temperature.

Waterloo made an attempt to activate the BPL catalyst by calcining it in an inert atmosphere at 400 °C for 2 h. However, tests of this calcined catalyst at 21 °C showed no improvement in activity over the uncalcined catalyst.

The next step in an attempt to increase catalyst activity was to use more active catalysts at higher temperature (80 °C). These experiments were very successful as the results below will indicate.

Table 4. Effect of Inlet SO_2 Concentration on SO_2 Removal and Conversion at 21 °C on BPL Carbon (Cycle Time = 5 min; Flush Duration = 0.5 min)

Test no.	T6	T6 duplicate	T7	T8	T8 duplicate	T9
Inlet SO_2 conc. (ppmv)	2,500	2,500	1,810	1,215	1,215	600
Average SO_2 removal (%)	26.8	28.6	32.8	47.8	53.6	98.4
% SO_2 removed converted to H_2SO_4	23.7	26.7	69.1	88.0	83.2	98.9
Average acidity (mol/L)	0.008	0.008	0.007	0.006	0.007	0.007

Two catalysts were tested for SO₂ removal at 80 °C. One of these catalysts was a commercially promoted carbon catalyst modified by a proprietary activation procedure. This will be referred to hereafter as the modified carbon catalyst. Another catalyst was a CarboTech carbon catalyst (D52/4) supplied to us as 5 mm extrudes. This catalyst is potentially used in the Mitsui-BF SO_x/NO_x process.

The results of SO₂ removal at 80 °C using the modified carbon catalyst are shown in Table 5. The experiment was conducted using a 38.75 g (85 cc) bed of the modified carbon catalyst at a space velocity of 1,400 scc/(cc·h) with simulated flue gas containing 2,550 ppmv SO₂.

The cycle in Table 5 refers to the operation involving flue gas exposure followed by liquid flush. After this operation during each cycle, the bed was ready for the next exposure/cycle.

Except for cycle 1 and cycle 8, each of the cycles involved exposure of the bed at 80 °C to flue gas until a bed outlet SO₂ concentration (monitored by a continuous SO₂ analyzer) of 125 ppmv (~5% of inlet) was reached, followed by a liquid flush. The liquid flush was done off-line while maintaining the bed hot.

The results for SO₂ removal and acid strength achieved are highly promising as seen in Table 5. The catalyst shows no signs of deactivation and the cycle-to-cycle variations are believed to be due to the somewhat variable batch liquid flush procedure employed and not due to changes in catalyst.

The points of interest to note from Table 5 are as follows:

- The catalyst maintains over 97% SO₂ removal and high capacity with up to 4.32 N H₂SO₄ flushes, while producing up to 5 N H₂SO₄.
- When flushing liquid strength is increased to 8.31 N H₂SO₄, an 8.81 N H₂SO₄ is produced; however, the SO₂ removal drops to 64.5% for the next cycle.
- The loss of catalyst activity after the 8.31 N H₂SO₄ flush is reversible, i.e., the activity is restored by flushing again with lower strength solutions.
- The loss of catalyst activity with the higher strength acid flush is believed to be due to the lower solubility of O₂ in H₂SO₄. However, even with a 64.5% conversion, a two-bed trickle reactor process can be developed to produce nearly a 10 N H₂SO₄ while still achieving nearly 100% SO₂ removal. This concept has been described in our paper presented at the contractors' meeting last year.

The modified carbon catalyst system needs to be optimized further to achieve over 95% conversion at the highest possible throughput. It is believed that space velocities as high

Table 5. SO₂ Removal Test Results (38.75 g of Modified Carbon Catalyst, 80 °C, 1,400 scc/(cc-h) Flue Gas Containing 2,550 ppmv SO₂, 10% CO₂, 10% H₂O, 5% O₂, and Balance N₂)

Cycle	Breakthrough time (h) ^a	Percent SO ₂ removal	SO ₂ converted (g) ^b	Breakthrough extent ^c	Cold flushing liquid (200 cc)	Acid strength achieved, N
1	9.94	98.6	20.2	Complete	Water	1.02
2	5.76	>99.9	12.0	5%	Water	0.54
3	5.84	99.6	12.3	5%	Water	0.71
4	7.84	99.8	16.1	5%	4.32 N H ₂ SO ₄	5.24
5	4.04	99.8	8.4	5%	4.32 N H ₂ SO ₄	5.19
6	3.10	98.1	6.4	5%	4.32 N H ₂ SO ₄	4.94
7	3.60	99.6	7.4	5%	8.31 N H ₂ SO ₄	8.81
8	d	64.5	NA	NA	e	NA
9	2.5	99.3	5.3	5%	4.32 N H ₂ SO ₄	4.78
10	2.92	97.2	6.0	5%	4.32 N H ₂ SO ₄	5.08

^a5% breakthrough.

^bPer 100 g carbon at 5% breakthrough.

^cAt liquid flush.

^dConversion stayed constant at 64.5%. Run terminated after 3 h.

^e200 cc water followed by 200 cc 4.32 N H₂SO₄.

NA = Not analyzed.

as 10,000 scc/(cc·h) can be used. In the next quarter, the catalyst will be optimized further with respect to cost and effectiveness.

The second catalyst tested for SO₂ removal at 80 °C was the calcined CarboTech carbon (D52/4). NO_x conversion experiments described later show that this catalyst is significantly more active than the BPL carbon tested at 21 °C. Thus, this catalyst is expected to be more active than the BPL carbon for SO₂ oxidation as well.

The catalyst was supplied by CarboTech as 5 mm extrudes and 58.5 g was packed into the 85 cc bed. Following calcination at 400 °C for 2 h, only 51.7 g remained. This represents a weight loss of about 11.6% due to adsorbed water and organics.

The catalyst was then exposed to simulated flue gas at 80 °C in a manner similar to the modified carbon catalyst. In the first cycle exposure at 80 °C to flue gas containing 2,500 ppm SO₂, 99.3% removal was achieved and 5% breakthrough occurred after 2.22 h. A total of 3.62 g of SO₂ was removed per 100 g of carbon. In using a 4.32 N H₂SO₄ flush solution, 4.52 N H₂SO₄ was achieved.

In the second cycle, the highest conversion observed over a 2.4-h period was 50%. In using pure water as the flushing liquid, 0.93 NH₂SO₄ was obtained.

In the third cycle, the highest conversion observed over a 2.24-h period was 49%. It appears that once the CarboTech carbon was flushed with 4.32 H₂SO₄, its activity for SO₂ removal was reduced and its activity is not as high as the modified carbon catalyst. However, its activity appears to be much higher than the Calgon BPL carbon. The CarboTech and the Calgon materials need to be tested under identical conditions to confirm this.

The modified carbon catalyst appears to be highly promising for SO₂ removal and, as indicated earlier, will be further optimized in the next quarter. Also the effect of NO_x on the SO₂ removal process will be studied.

3.3 NO_x REMOVAL

A number of catalysts have been screened to date as a function of process variables. A catalyst, hereafter referred to as the modified carbon catalyst, gave very promising results. Results of all catalysts to date except the modified carbon catalyst are summarized in Table 6. The results of the modified carbon catalyst are presented in Figures 4 to 6.

The results show that the calcined CarboTech carbon and the platinum-promoted Degussa carbons were found to be active for NO-NH₃ reaction but not as active as the modified carbon catalyst. The results also indicate that the conversion of NO requires about 1.5 mol of NH₃ for every mol of NO, since the conversions begin to be limited by the near extinction of NH₃ at high conversion levels and the NH₃/NO mol ratio is less than 1.5.

Table 6. NO_x Conversion Test Results

Catalyst	Bed size (g)	Bed volume (cc)	Bed I.D. (cm)	Space velocity (scc/(cc h))	Temperature (°C)	NO in (ppmv)	NH ₃ /NO (nominal)	NO conversion (%)
Uncalcined Calgon BPL 10x16	12	27	2.1	8274	150	420	1.25	0
	12	27	2.1	4467	150	350	1.43	2.9
	12	27	2.1	4422	98	400	1.26	7.5 ^a
Uncalcined Calgon BPL 6x16	52	110	3.4	1081	150	530	1.00	18.9
	52	110	3.4	1086	104	505	1.03	26.7 ^a
Uncalcined Calgon BPL 4x6	42.3	85	3.0	1412	82	500	1.03	29.0 ^a
	42.3	85	3.0	1412	152	500	1.03	24.0
Degussa 0.5% Pt/Carbon, 2.5 - 4.5 mm	37.8	85	3.0	1419	82	470	1.06	36.2 ^a
	37.8	85	3.0	1419	153	470	1.06	55.3 ^b
	37.8	85	3.0	1384	121	470	1.06	14.9
	37.8	85	3.0	1390	137	480	1.04	33.3
	37.8	85	3.0	1390	153	480	1.04	56.2 ^b
	37.8	85	3.0	1390	168	480	1.04	58.3
Degussa 1.0% Pt/Carbon, 2.5 - 4.5 mm	38.8	85	3.0	1412	82	485	1.03	35.1 ^a
	38.8	85	3.0	1412	153	485	1.03	55.7 ^b
	38.8	85	3.0	1390	122	490	1.02	23.5 ^a
	38.8	85	3.0	1390	137	490	1.02	46.9
	38.8	85	3.0	1390	168	490	1.02	61.2 ^b
Uncalcined Calgon BPL 18x20	41.3	85	3.0	1376	122	480	1.04	17.7 ^a
	41.3	85	3.0	1376	137	480	1.04	16.7
	41.3	85	3.0	1376	152	480	1.04	14.6
	41.3	85	3.0	1376	167	480	1.04	14.6
Uncalcined CarboTech D52/4 3/16" extrudes	49.5	85	3.0	1369	123	460	1.09	39.1 ^a
	49.5	85	3.0	1369	137	460	1.09	37.0
	49.5	85	3.0	1369	152	460	1.09	37.0
	49.5	85	3.0	1369	166	460	1.09	37.0
Uncalcined CarboTech D52/4 5 mm extrudes	58.5	85	3.0	1400	140	530	1.22	32.0
	58.5	85	3.0	1400	150	530	1.22	35.0
	58.5	85	3.0	1400	160	530	1.22	40.0
Calcined Calgon BPL 4x6	41.1	85	3.0	1400	139	530	1.22	16.0
	41.1	85	3.0	1400	150	530	1.22	17.0
	41.1	85	3.0	1400	160	530	1.22	19.0
Calcined Carbotech D52/4 5 mm extrudes	51.7	85	3.0	1400	130	530	1.22	50.0
	51.7	85	3.0	1400	140	530	1.22	50.0
	51.7	85	3.0	1400	150	530	1.22	52.5
	51.7	85	3.0	700	160	530	1.22	66.0 ^b
	51.7	85	3.0	700	150	530	1.22	67.0 ^b
	51.7	85	3.0	700	167	530	1.22	69.0 ^b

^aResult could be influenced due to adsorption which is dominant below 120 °C.

^bConversion could be limited due to unavailability of sufficient NH₃.

Figure 4. NO conversion on modified carbon catalyst
(space velocity = 1370 scc/(cc·h)
[3005 scc/(g·h)]; inlet NO = 530 ppmv)

Figure 5. NO conversion on modified carbon catalyst
(space velocity = 1370 scc/(cc·h)
[3005 scc/(g·h)]; inlet NO = 530 ppmv;
 $\text{NH}_3/\text{NO} = 1.42$)

The NO_x removal data shown in Figures 4 to 6 for the modified carbon catalyst were taken during a 267-h longevity test of this catalyst. The catalyst has shown no signs of deactivation after this long-term test. The data show that the required 75% removal with 25 ppmv NH_3 slip can be obtained on this catalyst at a space velocity of about 1,300 to 1,800 scc/(cc·h) [3,000 to 4,000 scc/(g·h)], at 135 to 140 °C, with an NH_3 to NO_x inlet ratio of about 1.25. No NO_2 or other nitrogen products were detected in the outlet and the reaction suggested an overall stoichiometry in which nearly 1.5 mol of NH_3 was consumed for every mol of NO fed.

Recent data to be reported next quarter show that further optimization of this family of catalysts is possible at an NH_3/NO ratio of ~1.42. A significantly lower level of promoter is adequate which minimizes catalyst cost and therefore lower temperatures are usable. In addition, space velocities as high as 3,000 scc/(cc·h) [6,600 scc/(g·h)] gave up to 90% conversion with little NH_3 slip. It is expected that space velocities as high as 10,000 scc/(cc·h) [22,000 scc/(g·h)] or higher can be used while still meeting the targets for NO_x conversion and NH_3 slip.

Selected results of the catalysts shown in Table 6 are compared to those of the modified carbon catalyst from Figure 4 in Figure 7.

The following observations are noteworthy:

- None of the carbon catalysts except the modified carbon catalyst displayed NO_x efficiency which was sensitive to temperature. Thus, the rate of NO_x conversion is limited by diffusion on the carbon catalysts but appears to be kinetically limited on the modified carbon catalyst.
- The calgon BPL carbon was the least active catalyst for NO_x conversion.
- The uncalcined CarboTech carbon (potentially used in the Mitsui-BF process) can be activated by calcination to give higher conversion.
- The calcined CarboTech gave slightly higher conversion than the modified carbon catalyst at 130 °C. However, the modified carbon catalyst was best overall and gave higher conversion at above 132 °C than the CarboTech carbon.

In the future, the modified carbon catalyst will be further optimized for NO_x removal. Also, the effect of traces of SO_2 on the NO_x removal process will be studied.

Figure 6. NO conversion on modified carbon catalyst
(Space velocity = 1758 scc/(cc·h)
[3948 scc/(g·h)]; Inlet NO = 530 ppmv;
NH₃/NO = 1.25)

Figure 7. NO conversion on various carbon-based catalysts (85 cc bed; 1400 scc/(cc·h); 15.7 psia; 5% O₂, 10% CO₂, 10% H₂, 75% Inert; 530 ppm NO in; NH₃/NO = 1.22)

4.0 WORK PLANNED FOR NEXT QUARTER

4.1 SO₂ REMOVAL

Partial factorial experiments will be conducted at Waterloo at 21 °C with BPL carbon and modified carbon catalysts. The modified carbon catalyst will be further optimized at 80 °C with respect to throughput, acid strength, and promoter level. The effect of NO_x on the SO₂ removal process will be studied.

4.2 NO_x REMOVAL

The modified carbon catalyst will be optimized further with respect to throughput and promoter level. The effect of traces of SO₂ on the NO_x removal process will be studied.

4.3 PROCESS EVALUATION AND PUBLICATIONS

A preliminary economic evaluation of the process will be conducted. A project review meeting will be held on May 4, 1992. Papers will be presented at the PETC contractors' review meeting and the Minneapolis AIChE meeting.

5.0 REFERENCES

- Hartman, M., and R.W. Coughlin. 1972. *Chem. Eng. Sci.* 127:867-880.
- Harman, M., J. Polek, and R.W. Coughlin. 1971. *Chem. Eng. Prog. Symp. Ser.*, No. 115, 67:7-22.
- Haure, P., R.R. Hudgins, and P.L. Silveston. 1989. *AIChE Journal*, 35:1437.
- Kareko, K., Y. Nakahigashi, and K. Nagata. 1988. *Carbon*, 26(3):327-333.
- Keuhl, H., E. Richter, K. Knoblauch, and H. Juentgn. 1986. *Carbon '86, Bergan-Forschung*, Essen, Germany, pp. 351-353.
- Kusakube, K., M. Karhima, S. Morook, and K. Shigeharu. 1988. *Fuel*, 67(5):714-718.
- Seki, M., Y. Sakurai, and K. Yoshida. 1975. *Am. Chem. Soc. Div. Eng. Chem. Reprints*: 15(2), Chicago Meeting, August 24-29, pp. 28-31.

END

**DATE
FILMED**

8 / 28 / 92